

**ISTC 2171**

**Final  
Project Technical Report  
of ISTC 2171**

**Fundamental Research on Combustion of Organophosphorous Esters and  
Synthesis of Promoting Additives**

**(From 1 September 2002 to 31 August 2002 for 12 months)**

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<b>14. ABSTRACT</b>  This report results from a contract tasking Institute of Physiologically Active Compounds as follows: Burning velocities and flammability limits for gaseous organophosphorous esters (OPE)/air mixtures, as well as effects of fluorine-containing additives on the burning velocities and flammability limits, will be determined. Fluorine-containing additives which promote combustion of OPE/air mixtures will be synthesized.					
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Fundamental Research on Combustion of Organophosphorous Esters and Synthesis of  
Promoting Additives

(From 1 September 2002 to 31 August 2002 for 12 months)

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An experimental facility for measuring the burning velocities and concentration flammability limits for gaseous fuel/air mixtures was designed and constructed. Velocities of burning are determined for stoichiometric dimethyl ester of vethylphosphonic acid/air and triethylphosphate/air mixtures are 0.24 m/s and 0.31 m/s, respectively. Influence of the fluorocontaining additives ( $\text{NF}_3$ ,  $\text{N}_2\text{F}_4$ ,  $\text{SF}_6$ ,  $\text{F}_5\text{S-R}$ ) on the speed and concentration limits of burning of phosphorus organic ester / air mixes is established. The addition of  $\text{NF}_3$  and  $\text{N}_2\text{F}_4$  increases the OPE burning velocities and expands the flammability ranges for phosphorus organic ester. The addition of  $\text{F}_5\text{S-R}$  reduces the OPE burning velocities and expands the flammability ranges for phosphorus organic ester. The addition of  $\text{SF}_6$  reduces the OPE burning velocities and flammability ranges for phosphorus organic ester.

Was established that interaction of sulfur chloride pentafluoride ( $\text{F}_5\text{SCl}$ ) and unsaturated alcohols under irradiation of ultra-violet light leads to adducts of addition of  $\text{F}_5\text{SCl}$  to the double bounds in good yields. These adducts are useful precursors in the preparation of novel compounds containing pentafluorothio groups. For the first time shown, that realization of reaction addition of sulfur chloride pentafluoride ( $\text{F}_5\text{SCl}$ ) in the condition of photochemical or thermal reaction of addition, leads to formation of high strained cyclic compounds with sulfur pentafluoride groups ( $\text{F}_5\text{S}$ ) in good yield. Effective way of synthesis of mono- and di- adducts of  $\text{SF}_5\text{Cl}$  and 1,4-, and 1,5-alkadienes was found. These adducts are useful precursors in the preparation of earlier not known 1,3-, 1,4- and 1,5-alkadienes with sulfur pentafluoride groups.

Key words: burning, burning velocities, phosphorus organic ester, fluoroorganic compounds.

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## 1. Introduction.

Purpose of the project: determination of burning velocities and flammability limits of mixture of organophosphorous esters with air, and syntheses of SF<sub>5</sub>-containing materials (or composition) which have promoting effect on ignition/combustion of various derivatives of phosphorus acid.

Working-plan of project 2171 consists of two basic stages

- research of process of burning organophosphorous esters.
- synthesis of cyclic and acyclic compounds containing pentafluorosulfanyl (SF<sub>5</sub>) group.

Researches of the first stage include:

- 1) experimental investigation of burning velocities and flammability limits for gaseous dimethyl ester of methylphosphonic acid /air and triethylphosphate /air mixture;
- 2) Experimental investigation of the effects of fluorine-containing additives (SF<sub>5</sub>-R, SF<sub>6</sub>, NF<sub>3</sub>, N<sub>2</sub>F<sub>4</sub>) on the burning velocities and flammability limits of dimethyl ester of methylphosphonic acid/air and triethylphosphate/air mixtures.

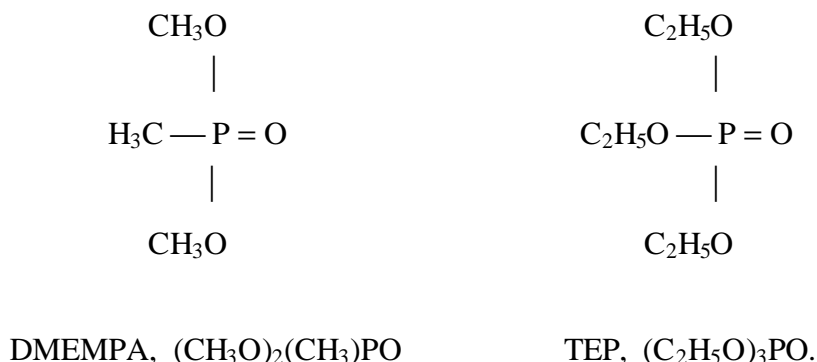
Researches of the second stage include:

- 1) Development of synthetic methods for the introduction of pentafluorosulfanyl (SF<sub>5</sub>) fragment into unsaturated alcohols:
  - under pressure
  - photochemical reaction.
- 2) Development of synthetic methods for the introduction of pentafluorosulfanyl (SF<sub>5</sub>) fragment into strained compounds containing double bonds:
  - under pressure
  - photochemical reaction.
- 3) Study reaction of pentafluorosulfanyl chloride with 1,4- and 1,5-alkadienes:
  - photochemical reaction.

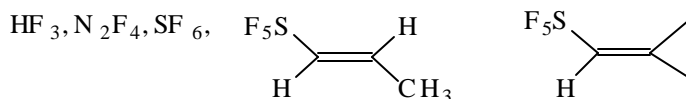
## 2. Research of process combustion of organophosphorous esters.

The present part of final report of summarizes the results obtained during implementation of tasks concerning experimental investigation of the burning velocities and flammability limits for gaseous mixtures of organophosphorous esters (OPEs), with air and of the effects of fluorine-containing additives on the velocities and the limits.

The studied OPEs were dimethyl ester of methylphosphonic acid (DMEMPA), and triethylphosphate (TEP):



The studied fluorine-containing additives were:



### 2.1. Experimental Facility and Technique

Experiments were carried out in a facility schematically shown in Fig. 2.1.1. The facility consisted of a 4-cm ID x 18-cm length combustion chamber (1) supplied with a valve (2) for chamber evacuating and filling with the combustible mixture to be studied. The mixture was prepared in a 1.2-L mixer (3) supplied with a propeller for fast mixing. The mixture in the chamber was ignited by an electric spark (4). A pressure history during combustion of the mixture was recorded by a quartz pressure gauge (5) with the following digitizing on a digital oscillograph (10) and data processing on a computer (11).

A method of processing was as follows. For combustion in a constant volume chamber holds

$$DP/DP_{\max} = Dm/m_0, \quad (2.1)$$

where  $DP$  and  $DP_{\max}$  correspond to the current and maximum pressure increases during combustion, and  $Dm$  and  $m_0$  correspond to the burned and initial mixture masses, respectively. Differentiation of (2.1) with respect to time in view of  $d(Dm)/dt = SrV$  and  $m_0 = Sr_0L$ , where  $V$  is the burning velocity,  $S$  is the chamber cross section,  $L$  is the chamber length,  $r_0$  and  $r$  correspond to the initial mixture density and the preflame one, gives

$$V = L(r_0/r)d(DP/DP_{\max})/dt. \quad (2.2)$$

Taking into account that  $r_0/r = (P/P_0)^{-1/\gamma}$ , we got from (2.2)

$$V = L(P/P_0)^{-1/\gamma}d(DP/DP_{\max})/dt. \quad (2.3)$$

Equation (2.3) allows one to determine the burning velocity from the measured pressure and pressure derivative during combustion.

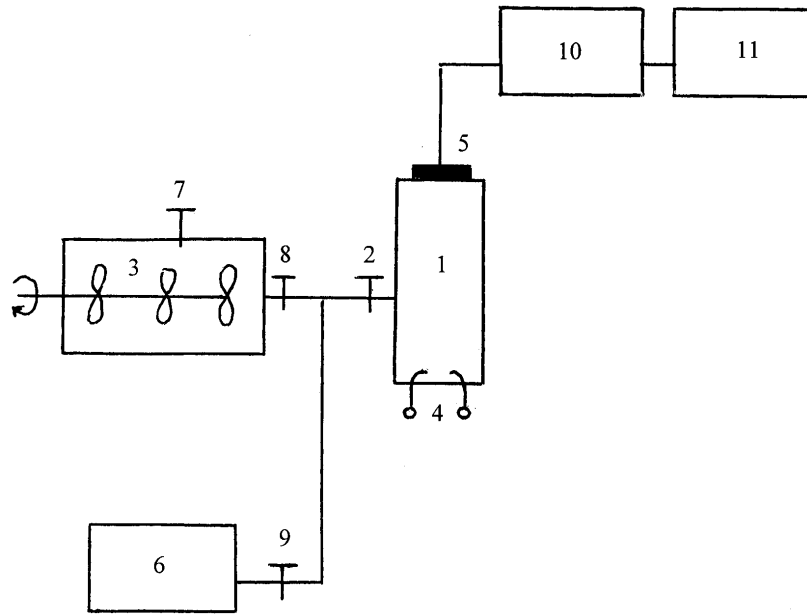


Fig. 2.1.1.

Schematic of a facility for measuring the burning velocities and concentration flammability limits for gaseous fuel/air mixtures:

(1) combustion chamber; (2) valve; (3) mixer; (4) electric spark; (5) pressure gauge; (6) pump; (7) – (9) valves; (10) digital oscillograph; (11) computer.

## 2.2. Approbation of the Technique

To estimate the accuracy of the proposed technique for measuring the burning velocity, we studied the combustion of the stoichiometric propane/air mixture and compared the measured burning velocity with the tabulated one. Figures 2.2.1 and 2.2.2 show time histories for pressure increase and pressure derivative during combustion of the mixture at initial room temperature and atmospheric pressure. Figure 2.2.2. shows that there are four stages of flame propagation in the chamber.



Stage 1 is characterized by flame acceleration due to turbulence generation in the preflame zone. The turbulence is generated by the propagating flame front which acts as a moving piston that accelerates a gas in front of it.

Stage 2 is characterized by flame deceleration due to turbulence decay in the preflame zone. The decay is explained by deceleration of the flame piston due the compression of combustion products behind it. So, Stages 1 and 2 are those of turbulent combustion.

Stage 3 is that of laminar combustion as it takes place after the turbulence decay. Here, the flame acceleration is associated with compression-induced increase in preflame gas temperature.

Stage 4 is the final one of combustion. Here, the deceleration of the flame is explained by heat losses.

In this way, it is Stage 3 only that can be used for determining the laminar burning velocity. The use of Eq. (2.3) for processing Stage 3 gave the curve of  $V(t)$  (see Fig. 2.2.3). Combining the  $V(t)$  and  $P(t)$  curves, we obtained  $V(P/P_0)$  as a linear log–log plot<sup>\*)</sup> (see Fig. 2.2.4). Extrapolating the line to  $P/P_0 = 1$ , we determined the laminar burning velocity at atmospheric pressure,  $V(\text{exptl.}) = 0.36 \text{ m/s}$ . For comparison, the tabulated burning velocity for the stoichiometric  $\text{C}_3\text{H}_8/\text{air}$  mixture is  $0.39 \text{ m/s}$  at atmospheric pressure,  $V(\text{tabl.}) = 0.39 \text{ m/s}$ . The difference between the measured and tabulated burning velocities is 7.7 %.

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<sup>\*)</sup>As depending on preflame pressure and temperature, the laminar burning velocity has the form

$$V = V_0(P/P_0)^{a1}(T/T_0)^{a2}. \quad (\text{A1})$$

For adiabatic compression of preflame gas holds

$$T/T_0 = (P/P_0)^{(\gamma-1)/\gamma}. \quad (\text{A2})$$

Substituting (A2) into (A1) gives

$$V = V_0(P/P_0)^{a3}. \quad (\text{A3})$$

This means that the  $\log(V)$  plotted versus  $\log(P/P_0)$  is a line.

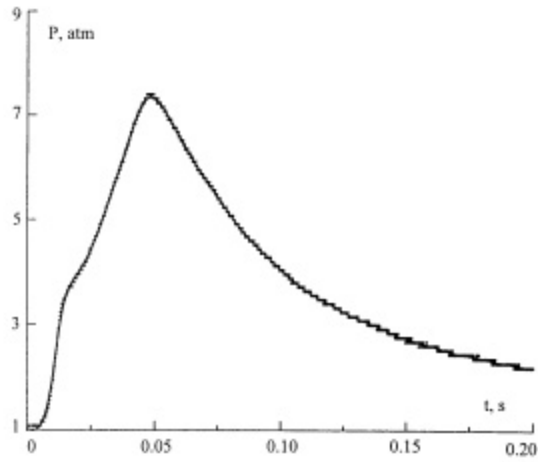


Fig. 2.2.1.

Time history for pressure increase during combustion of the stoichiometric C<sub>3</sub>H<sub>8</sub>/air mixture at initial room temperature and atmospheric pressure.

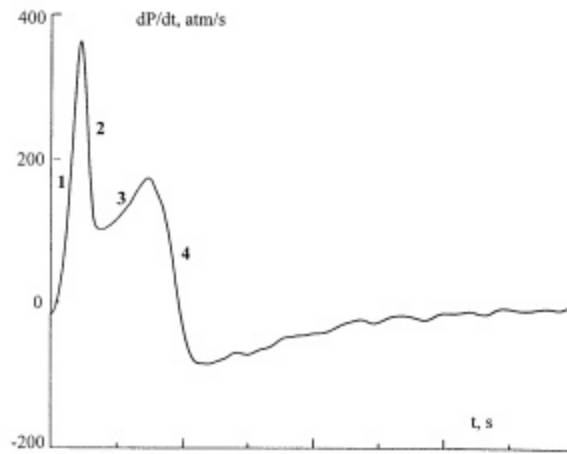


Fig. 2.2.2.

Time history for pressure derivative during combustion of the stoichiometric C<sub>3</sub>H<sub>8</sub>/air mixture at initial room temperature and atmospheric pressure: (Stage 1 is that of flame acceleration due to turbulence generation in the preflame zone; Stage 2 is that of flame deceleration due to turbulence decay in the preflame zone; Stage 3 is that of laminar combustion; Stage 4 is the final one).

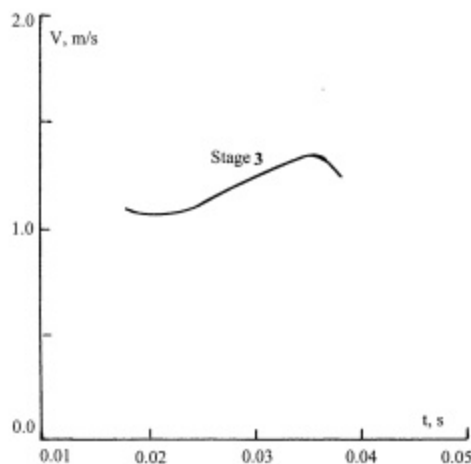


Fig. 2.2.3.

Burning velocity versus time for combustion of the stoichiometric  $\text{C}_3\text{H}_8/\text{air}$  mixture during the stage of laminar combustion, (Stage 3 in Fig. 2.2.2.)

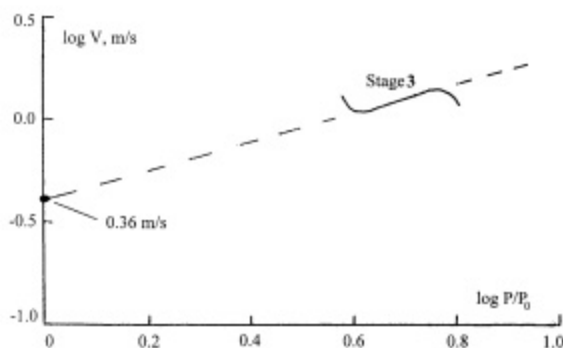


Fig. 2.2.4.

Logarithmic burning velocity versus logarithmic pressure for combustion of the stoichiometric  $\text{C}_3\text{H}_8/\text{air}$  mixture during the stage of laminar combustion, Stage 3 in Fig. 2.2.2.

The plot of  $\log(V)$  versus  $\log(P/P_0)$  is a line. Extrapolation of the line to  $P/P_0 = 1$  gives the laminar burning velocity at atmospheric pressure,  $V(\text{exptl.}) = 0.36 \text{ m/s}$ .

Figure 2.2.5 shows the burning velocity versus equivalence ratio,  $j$ , measured for  $\text{C}_3\text{H}_8/\text{air}$  mixtures by using the proposed technique. It follows from Fig. 2.2.5 that the mixtures are combustible within the range  $0.58 < j < 2.36$ . This means that the measured lean and rich concentration flammability limits are  $j_l(\text{eptl.}) = 0.58$  and  $j_r(\text{eptl.}) = 2.36$ , respectively. The

tabulated lean and rich concentration flammability limits are  $j_l(\text{tabl.}) = 0.56$  and  $j_r(\text{tabl.}) = 2.47$ , respectively.

Table 2.2.1 compares the measured and tabulated burning velocities for the stoichiometric  $\text{C}_3\text{H}_8/\text{air}$  mixture, as well as the measured and tabulated lean and rich concentration flammability limits for  $\text{C}_3\text{H}_8/\text{air}$  mixtures. It follows from Table 2.2.1 that the difference between the measured and tabulated flame velocities does not exceed 10 %, whereas that between the measured and tabulated concentration flammability limits does not exceed 5 %. This validates the proposed technique for measuring the burning velocities and concentration flammability limits and allows us to use the technique for measuring the burning velocities and concentration flammability limits for gaseous mixtures of organophosphorous esters with air.

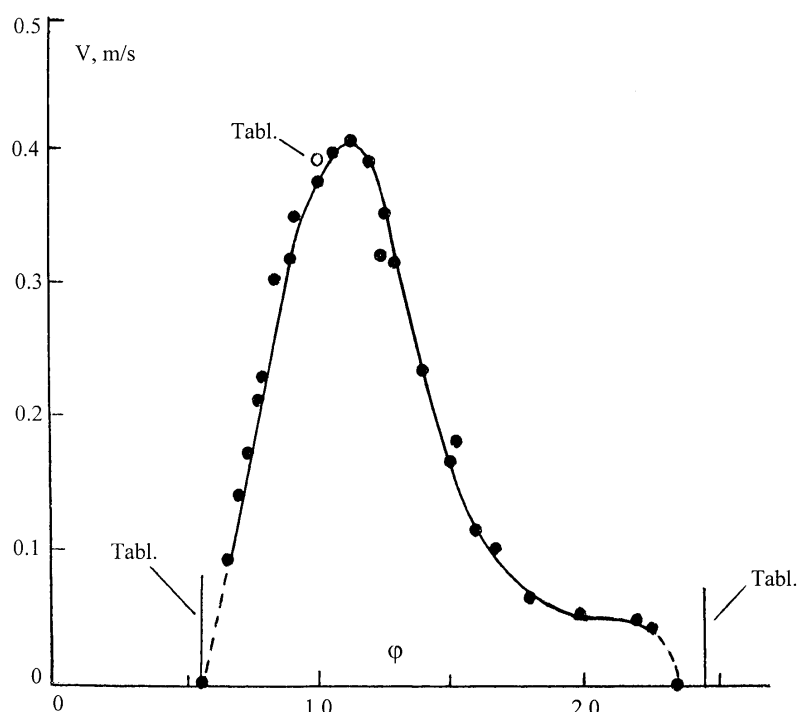


Fig. 2.2.5.

Burning velocity versus equivalence ratio for  $\text{C}_3\text{H}_8/\text{air}$  mixtures at initial room temperature and atmospheric pressure\*.

\* Black points correspond to the measured burning velocity, the light point corresponds to the tabulated burning velocity for the stoichiometric mixture.

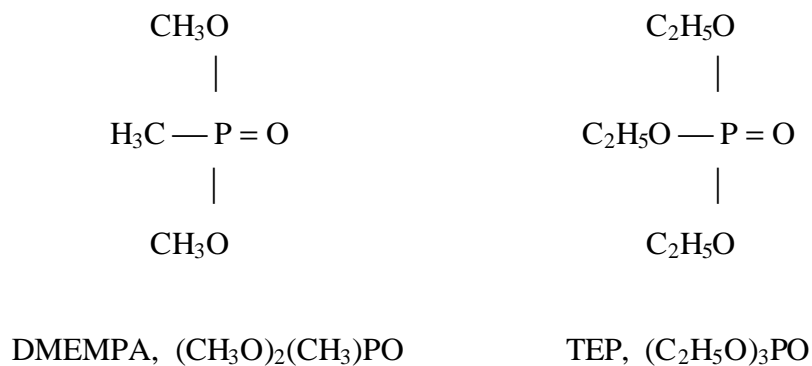
The mixtures are experimentally shown to be combustible within the range  $0.58 < j < 2.36$ . The tabulated lean and rich concentration flammability limits are 0.56 and 2.47, respectively.

**Table 2.2.1.** Comparison between the measured and tabulated burning velocities for the stoichiometric  $C_3H_8$ /air mixture, as well as the measured and tabulated lean and rich concentration flammability limits for  $C_3H_8$ /air mixtures.

	Measured	Tabulated	Accuracy
Burning velocity for $j = 1.0$	0.36 m/s	0.39 m/s	7.7 %
Lean concentration flammability limit, $j_l$	0.58	0.56	3.6 %
Rich concentration flammability limit, $j_r$	2.36	2.47	4.5 %

### 2.3. Burning Velocities and Concentration Flammability Limits for Gaseous Mixtures of Organophosphorous Esters with Air

In our experiments we used dimethyl ester of methylphosphonic acid (DMEMPA), and triethylphosphite (TEP), as examples of organophosphorous esters (OPEs),



Both DMEMPA and TEP are liquids at room temperature. To study the combustion of their gaseous mixtures with air, we electrically heated to 423 K both the mixer (3) and combustion chamber (1) of our facility shown in Fig. 2.1.1. This temperature ensured evaporation of the esters that allowed us to study the combustion of their gaseous mixtures with air. We also studied the combustion of propane/air mixtures at 423 K initial temperature for comparison. The technique for measuring the burning velocities and concentration flammability limits is described above. The results of the measurements are shown in Fig. 2.3.1.

Figure 2.3.1 shows the burning velocity,  $V$ , versus equivalence ratio,  $j$ , measured for DMEMPA/air, TEP/air, and propane/air mixtures at atmospheric pressure and 423 K initial temperature. It follows from the figure that the burning velocities for stoichiometric mixtures of DMEMPA, TEP, and propane with air are 0.24 m/s, 0.31 m/s, and 0.50 m/s, respectively. It also follows from Fig. 2.3.1 that the lean,  $j_l$ , and rich,  $j_r$ , concentration flammability limits are  $j_l = 0.58$  and  $j_r = 1.47$  for DMEMPA/air mixtures,  $j_l = 0.56$  and  $j_r = 1.64$  for TEP/air mixtures, and  $j_l = 0.52$  and  $j_r = 2.32$  for propane/air mixtures. These results are summarized in Table 2.3.1.

Table 2.3.2 gives the burning velocities for stoichiometric DMEMPA/air and TEP/air mixtures, as well as the lean and rich concentration flammability limits for DMEMPA and TEP, with

respect to those for propane. It follows from Table 2.3.2 that for the studied organophosphorous esters (i) the burning velocities are about twice lower than this value for propane, (ii) the lean concentration flammability limits are close to this value for propane, and (iii) the rich concentration flammability limits are less than this value for propane by a factor of about 0.65.

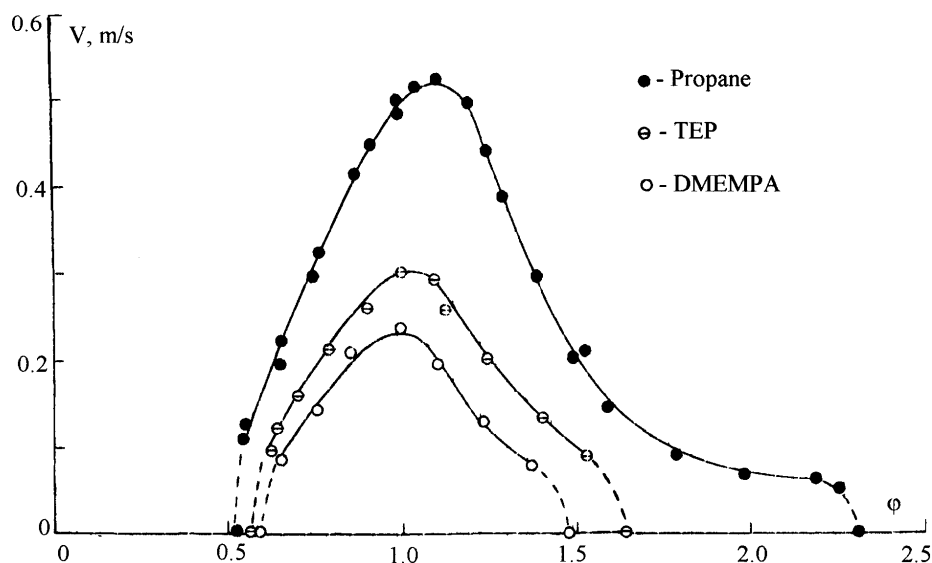


Fig 2.3.1.

Measured burning velocity versus equivalence ratio for DMEMPA/air and TEP/air gaseous mixtures at atmospheric pressure and 423 K initial temperature. The corresponding curve,  $V(j)$ , for propane/air mixture at the same pressure and initial temperature is shown for comparison.

**Table 2.3.1.** Measured burning velocities, as well as lean and rich concentration flammability limits for DMEMPA/air, TEP/air, and propane/air gaseous mixtures at atmospheric pressure and 423 K initial temperature.

	DMEMPA	TEP	Propane
Burning velocity for $j = 1.0^{*)}$	0.24 m/s	0.31 m/s	0.50 m/s
Lean concentration flammability limit, $j_l$	0.58	0.56	0.52
Rich concentration flammability limit, $j_r$	1.47	1.64	2.32

<sup>\*)</sup>Stoichiometric mixture

**Table 2.3.2.** Burning velocities, as well as lean and rich concentration flammability limits for DMEMPA/air and TEP/air gaseous mixtures at atmospheric pressure and 423 K initial temperature with respect to those values for propane/air mixtures at the same pressure and initial temperature.

	DMEMPA	TEP
$V_{j=1.0}(\text{OPE})/V_{j=1.0}(\text{propane})$	0.48	0.62
$j_L(\text{OPE})/j_L(\text{propane})$	1.12	1.08
$j_R(\text{OPE})/j_R(\text{propane})$	0.63	0.71

#### 2.4. Effects of Fluorine-Containing Additives on the Burning Velocities and Flammability Limits for Gaseous Mixtures of Organophosphorous Esters with Air

In our experiments we studied the effects of  $\text{NF}_3$ ,  $\text{N}_2\text{F}_4$ ,  $\text{SF}_6$ ,  $\text{F}_5\text{SCH}=\text{CH}-\text{CH}_3$ , and  $\text{F}_5\text{S}-\text{CH}=\text{cycloPr}$ , additives on the burning velocities and flammability limits for DMEMPA and TEP. In the experiments with  $\text{NF}_3$ ,  $\text{SF}_6$ ,  $\text{F}_5\text{SCH}=\text{CH}-\text{CH}_3$ , and  $\text{F}_5\text{S}-\text{CH}=\text{cycloPr}$  additives, the mixtures of OPEs, air and the additives were prepared in the mixer (3) of the facility shown in Fig. 2.4.1. The mixer was electrically heated to 423 K. This ensured evaporation both OPEs and  $\text{F}_5\text{S}-\text{R}$  additives which are liquids at room temperature. After their preparing, the mixtures were forwarded to the preliminarily evacuated chamber (1) and ignited by the electric spark (4). The chamber was also electrically heated to 423 K. In the experiments with the addition of  $\text{NF}_3$ , its mass percentages in air were 1.25, 2.5, and 5.0 wt %. In the experiments with  $\text{SF}_6$ ,  $\text{F}_5\text{SCH}=\text{CH}-\text{CH}_3$ , and  $\text{F}_5\text{S}-\text{CH}=\text{cycloPr}$  additives, their mass percentages in air were 2.5 and 5.0 wt %.

To avoid premature reaction between OPEs and highly-reactive  $\text{N}_2\text{F}_4$ , the mixtures with the addition of  $\text{N}_2\text{F}_4$  were prepared in two stages. At the first stage OPE/air mixtures were prepared in the mixer (3) electrically heated to 423 K, and  $\text{N}_2\text{F}_4$  was fed into the preliminarily evacuated chamber (1) which was also electrically heated to 423 K. At the second stage the OPE/air mixture was injected into the chamber through a 4-mm ID x 14-cm perforated tube (12) which was placed in the chamber as it is shown in Fig. 2.4.1. Fast mixing during the injection resulted in rapid formation of OPE/air/  $\text{N}_2\text{F}_4$  mixtures. The formed mixtures were then ignited by the electric spark (4). The mass percentage of  $\text{N}_2\text{F}_4$  in air was 5 wt. % in all experiments.

Pressure histories during combustion of OPE/air mixtures with fluorine-containing additives were recorded by a quartz pressure gage (5). Pressure records were processed to determine burning velocities and flammability limits. The technique for processing is described in Sections 2.2 and 2.3.

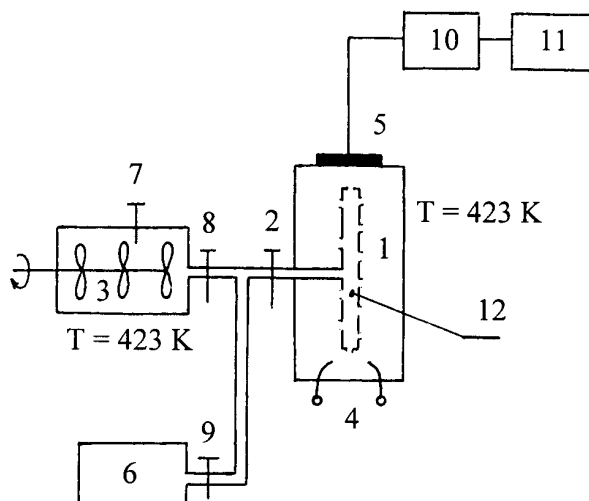


Fig. 2.4.1.

Schematic of a facility for measuring the burning velocities and concentration flammability limits for gaseous OPE/air/N<sub>2</sub>F<sub>4</sub> mixtures:

(1) combustion chamber; (2) valve; (3) mixer; (4) electric spark; (5) pressure gauge; (6) pump; (7) – (9) valves; (10) digital oscillograph; (11) computer; (12) perforated tube.

Experimental results on the burning velocities and concentration flammability limits for OPE/air mixtures with and without fluorine-containing additives are shown in Figs. 5.2–5.11.

Figures 2.4.2 and 2.4.3 show that the addition of NF<sub>3</sub> increases the burning velocities and expands flammability ranges for OPEs. Figures 2.4.4 and 2.4.5 show that the effects of N<sub>2</sub>F<sub>4</sub> addition on the OPE burning velocities and flammability limits are similar to those of NF<sub>3</sub> within the experimental error. Figures 2.4.6 and 2.4.7 show that the addition of SF<sub>6</sub> reduces the burning velocities and flammability ranges for OPEs. Figures 2.4.8 – 2.4.11 show that the addition of F<sub>5</sub>SCH=CH-CH<sub>3</sub> and F<sub>5</sub>SCH=cycloPr, reduces the OPE burning velocities and expands the flammability ranges for OPEs.



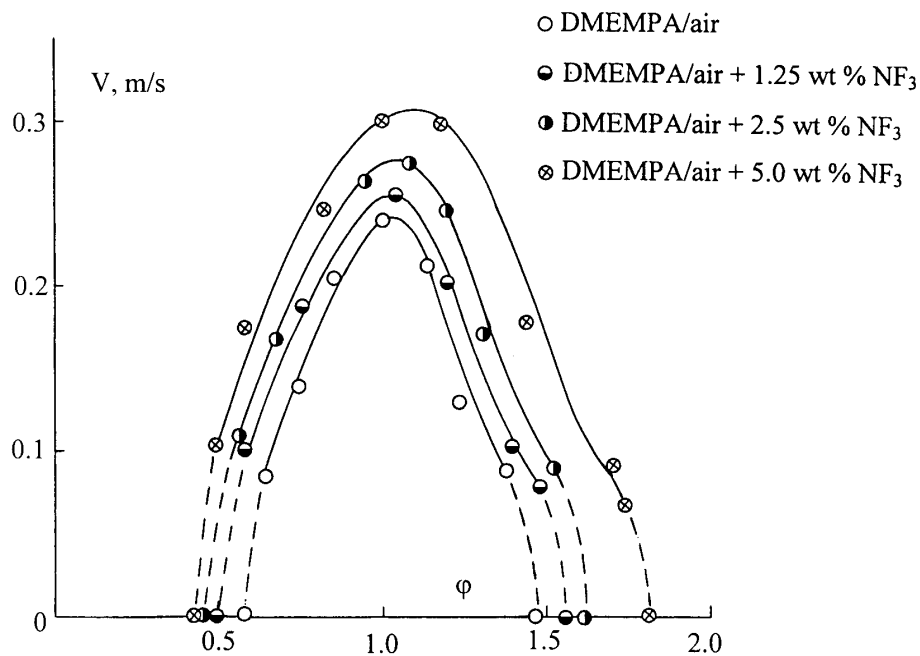


Fig. 2.4.2.

Effects of  $\text{NF}_3$  addition on the burning velocities and flammability limits for gaseous DMEMPA/air mixtures at atmospheric pressure and 423 K initial temperature.

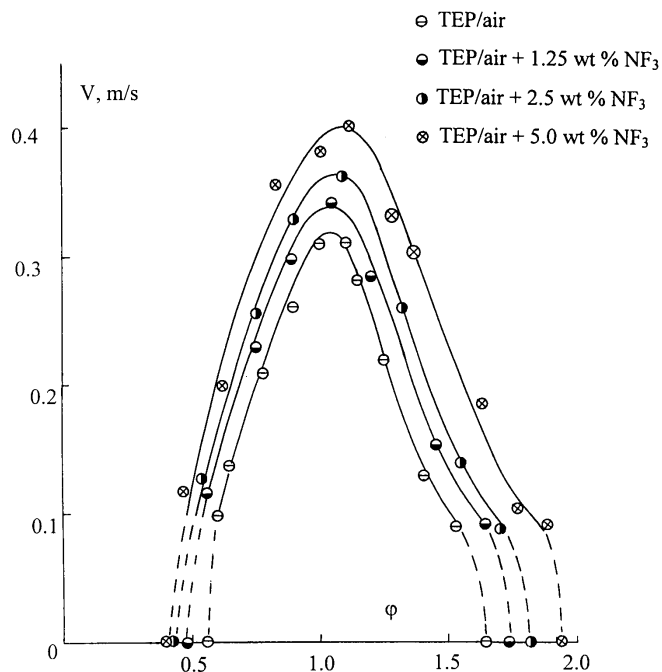


Fig. 2.4.3.

Effects of  $\text{NF}_3$  addition on the burning velocities and flammability limits for gaseous TEP/air mixtures at atmospheric pressure and 423 K initial temperature.

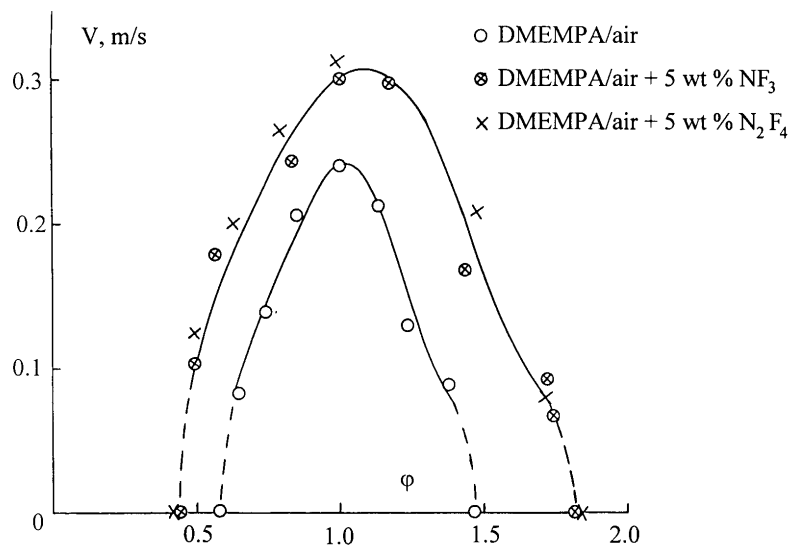


Fig. 2.4.4.

Comparison between the effects of  $\text{N}_2\text{F}_4$  and  $\text{NF}_3$  addition on the burning velocities and flammability limits for gaseous DMEMPA/air mixtures at atmospheric pressure and 423 K initial temperature.

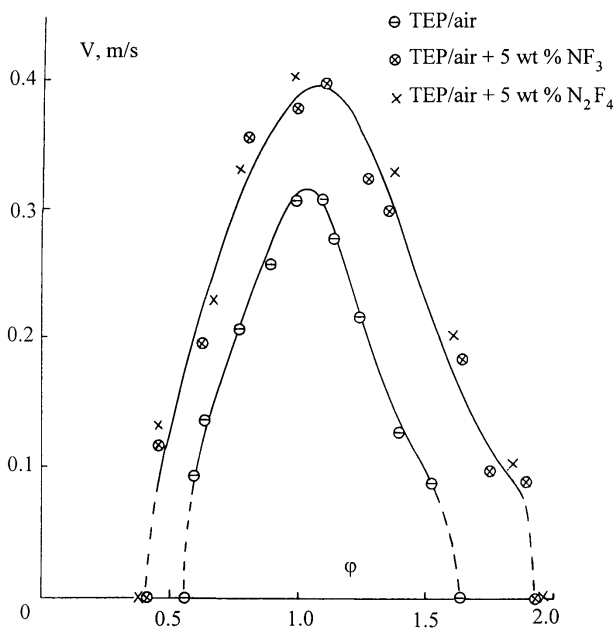


Fig. 2.4.5.

Comparison between the effects of  $\text{N}_2\text{F}_4$  and  $\text{NF}_3$  addition on the burning velocities and flammability limits for gaseous TEP/air mixtures at atmospheric pressure and 423 K initial temperature.

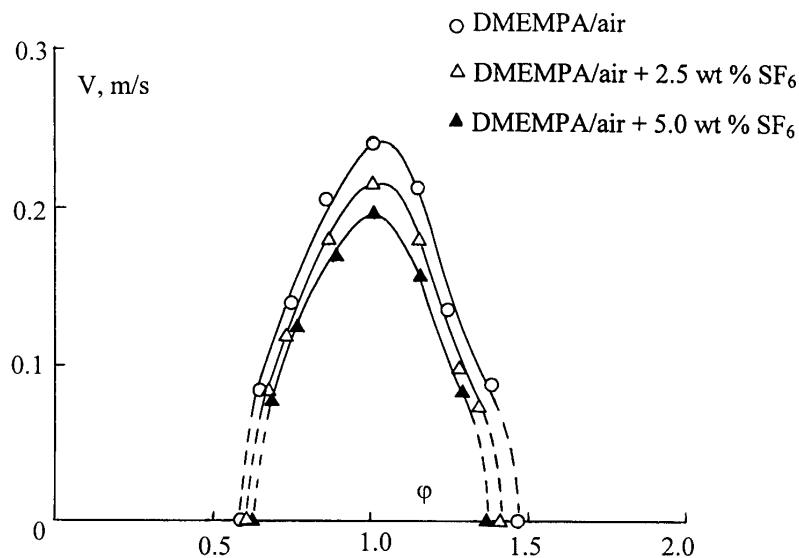


Fig. 2.4.6.

Effects of  $\text{SF}_6$  addition on the burning velocities and flammability limits for gaseous DMEMPA/air mixtures at atmospheric pressure and 423 K initial temperature.

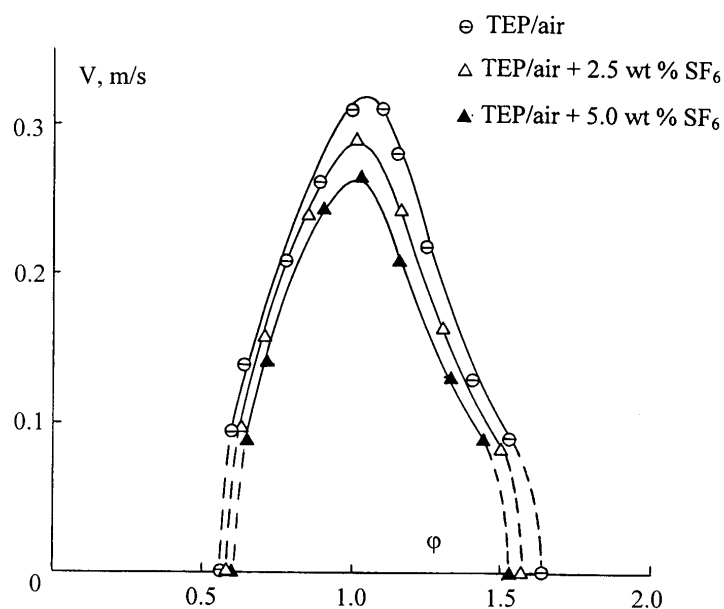


Fig. 2.4.7.

Effects of  $\text{SF}_6$  addition on the burning velocities and flammability limits for gaseous TEP/air mixtures at atmospheric pressure and 423 K initial temperature.

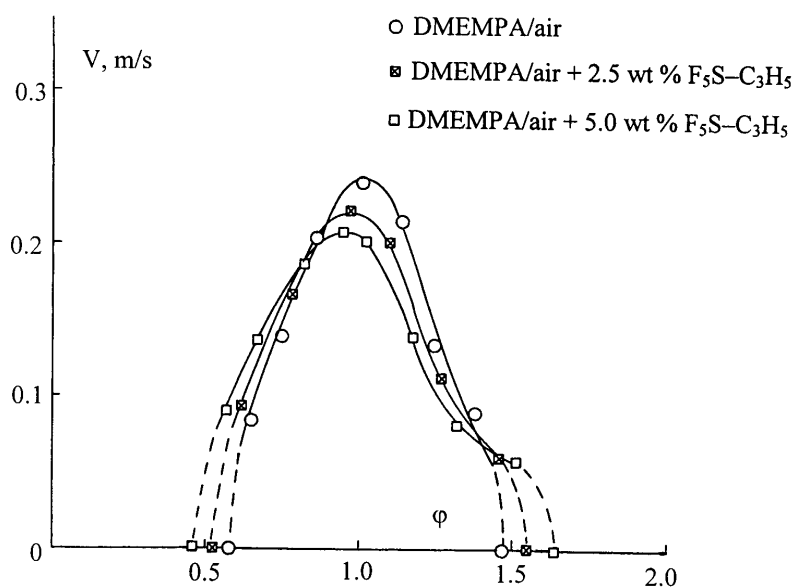


Fig. 2.4.8.

Effects of  $F_5SCH=CH-CH_3$  addition on the burning velocities and flammability limits for gaseous DMEMPA/air mixtures at atmospheric pressure and 423 K initial temperature.

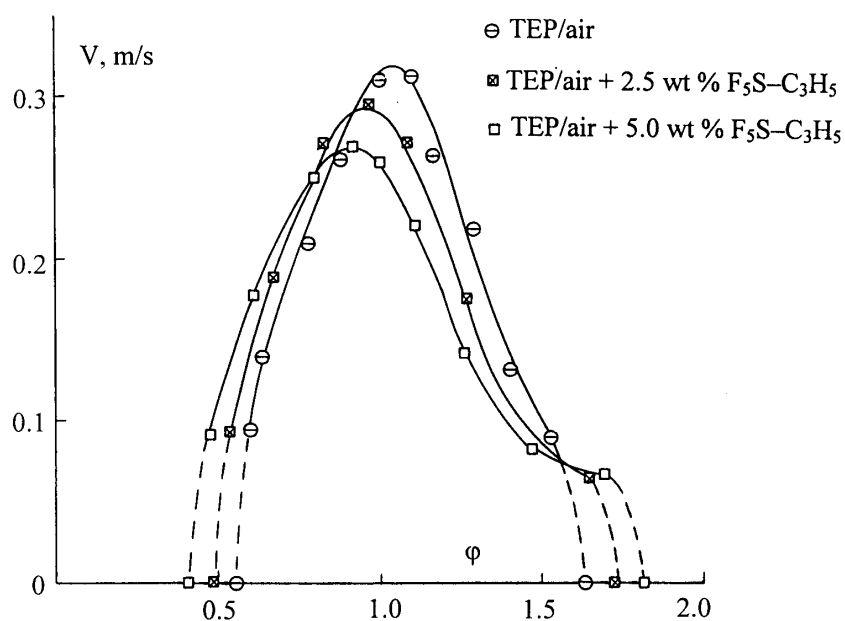


Fig. 2.4.9.

Effects of  $F_5SCH=CH-CH_3$  addition on the burning velocities and flammability limits for gaseous TEP/air mixtures at atmospheric pressure and 423 K initial temperature.

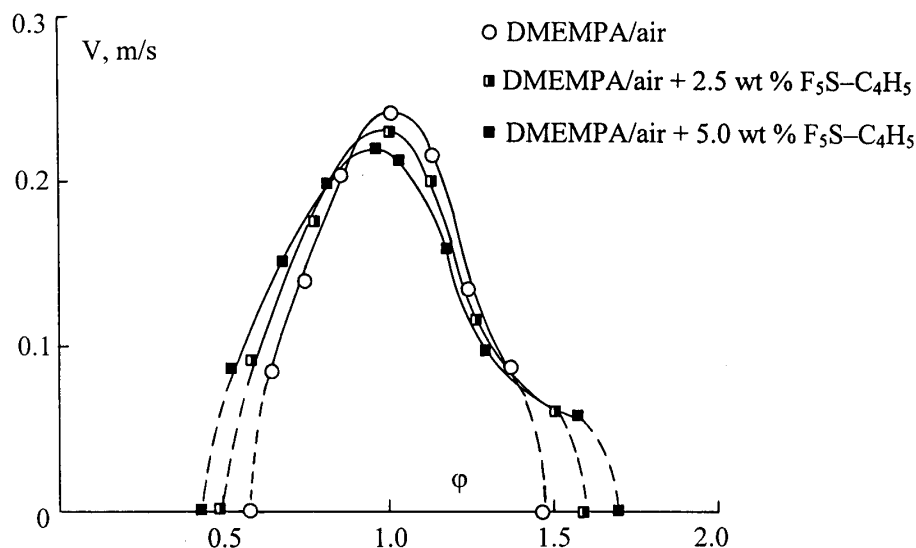


Fig. 2.4.10.

Effects of  $F_5SCH=cycloPr$  addition on the burning velocities and flammability limits for gaseous DMEMPA/air mixtures at atmospheric pressure and 423 K initial temperature.

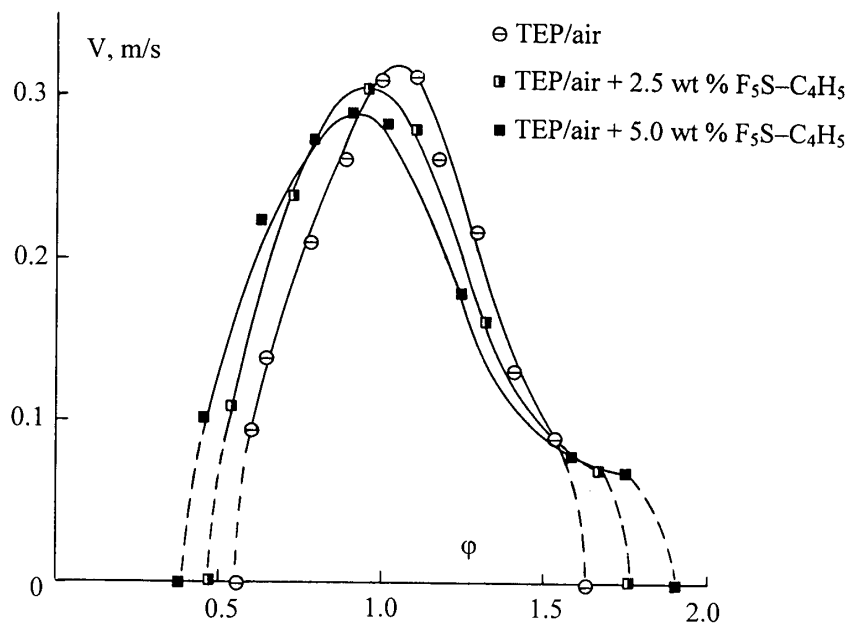


Fig. 2.4.11.

Effects of  $F_5SCH=cycloPr$  addition on the burning velocities and flammability limits for gaseous TEP/air mixtures at atmospheric pressure and 423 K initial temperature.

Figures 2.4.12 – 2.4.15 show the relative changes in the maximum burning velocities,  $V_m = \max V(\dot{j})$ , as well as the relative changes in the lean,  $\dot{j}_l$ , and rich,  $\dot{j}_r$ , concentration flammability limits for OPEs versus the mass percentage of the studied fluorine-containing additives in air, C. It follows from the Figures that the relative changes do not depend on the specific OPE within

the experimental error. Processing of the data presented in the Figures gave the following general correlations for the relative changes in the burning velocities and flammability limits:

1. Addition of  $\text{NF}_3$  and  $\text{N}_2\text{F}_4$ :

$$DV_m/V_m [\%] = 5.4 C [\%],$$

$$Dj_l/j_l [\%] = -10.0 C [\%] \text{ for } C < 2.5 \%,$$

$$Dj_l/j_l [\%] = -25.0 \text{ for } C \geq 2.5 \%,$$

$$Dj_r/j_r [\%] = 4.4 C [\%].$$

2. Addition of  $\text{SF}_6$ :

$$DV_m/V_m [\%] = -3.6 C [\%],$$

$$Dj_l/j_l [\%] = 0.6 C [\%],$$

$$Dj_r/j_r [\%] = -1.4 C [\%].$$

3. Addition of  $\text{F}_5\text{SCH}=\text{CH}-\text{CH}_3$ :

$$DV_m/V_m [\%] = -2.8 C [\%],$$

$$Dj_l/j_l [\%] = -5.0 C [\%],$$

$$Dj_r/j_r [\%] = 2.0 C [\%].$$

4. Addition of  $\text{F}_5\text{SCH}=\text{cycloPr}$ :

$$DV_m/V_m [\%] = -1.8 C [\%],$$

$$Dj_l/j_l [\%] = -6.0 C [\%],$$

$$Dj_r/j_r [\%] = 3.2 C [\%].$$

Table 2.4.1 compares the relative changes in the maximum OPE burning velocities and flammability limits due to the 5 wt % addition of fluorine-containing compounds to air. The table 2.4.1 shows that N- and F-containing additives increase the OPE burning velocities whereas S- and F-containing ones decrease the velocities.

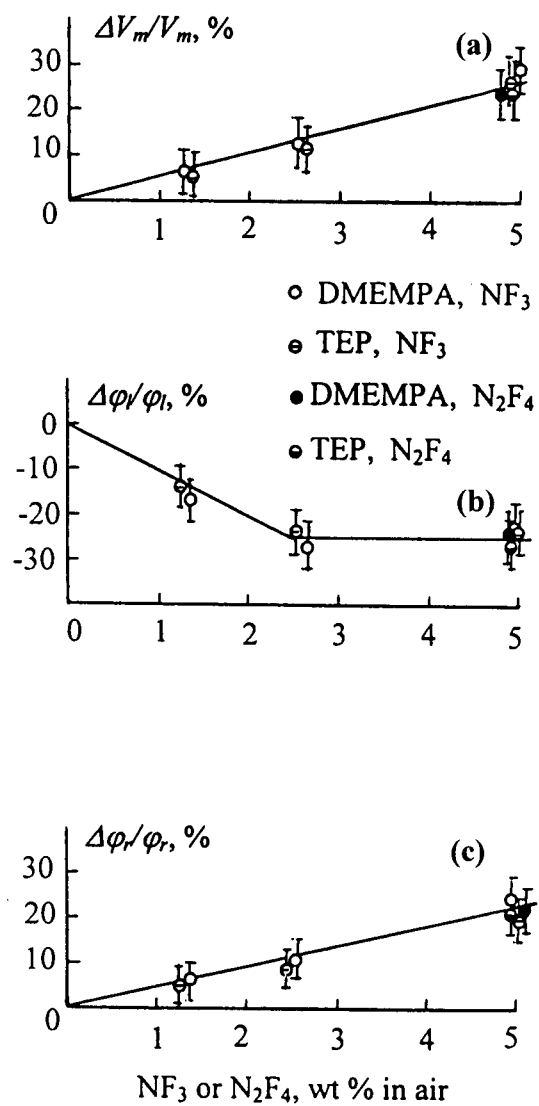


Fig. 2.4.12.

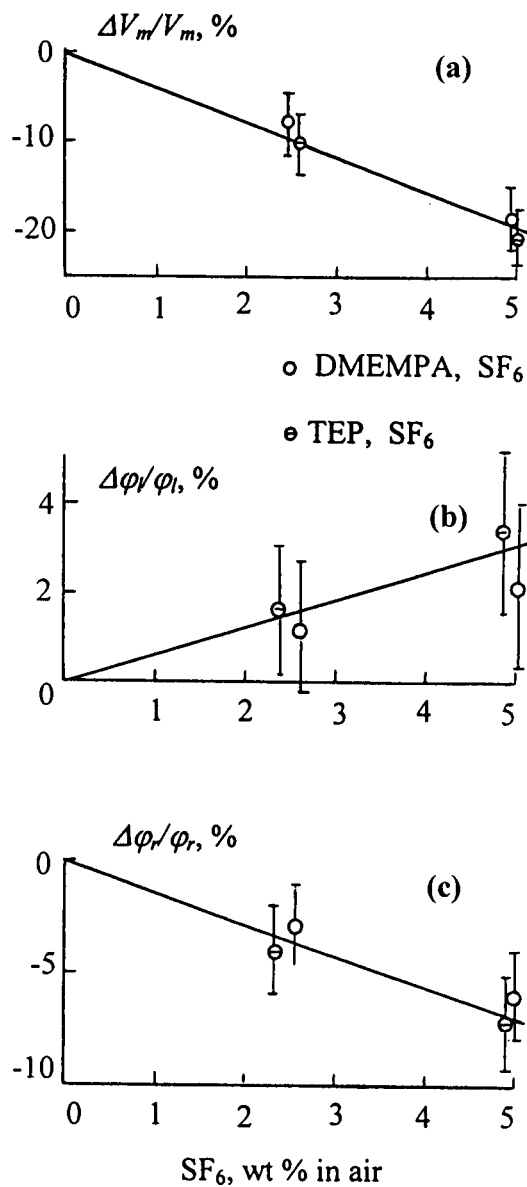


Fig. 2.4.13.

Relative changes in the maximum burning velocities,  $V_m = \max V(j)$  (a), and in the lean,  $j_l$  (b), and rich,  $j_r$  (c), concentration flammability limits for various OPEs versus the mass percentage of SF<sub>6</sub> in air.



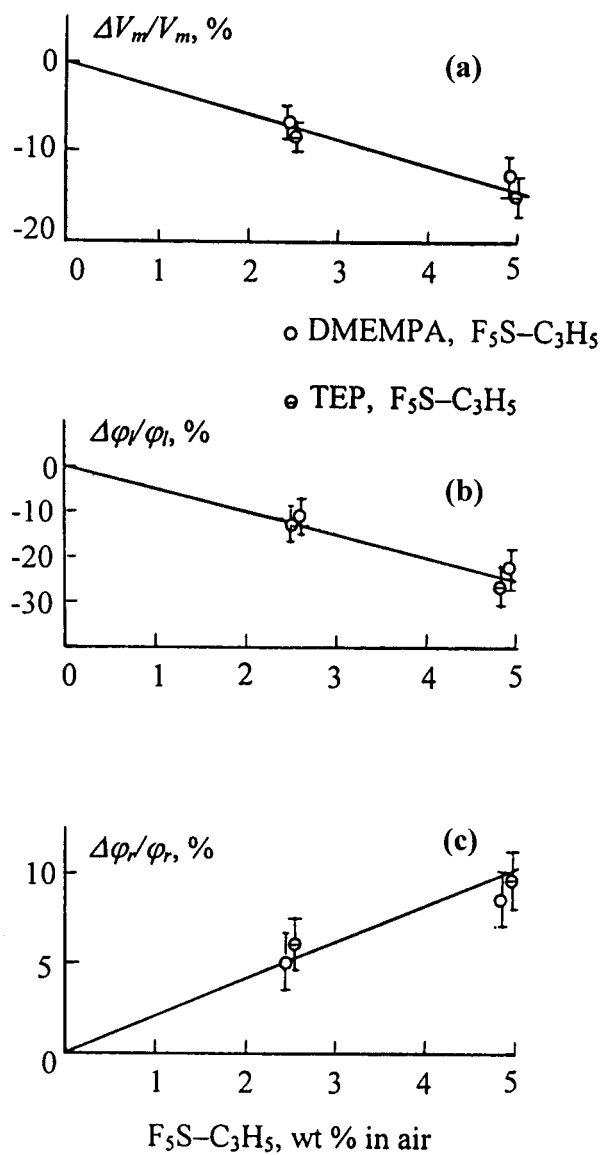


Fig. 2.4.14.

Relative changes in the maximum burning velocities,  $V_m = \max V(j)$  (a), and in the lean,  $j_l$  (b), and rich,  $j_r$  (c), concentration flammability limits for various OPEs versus the mass percentage of  $F_5SCH=CH-CH_3$  in air.

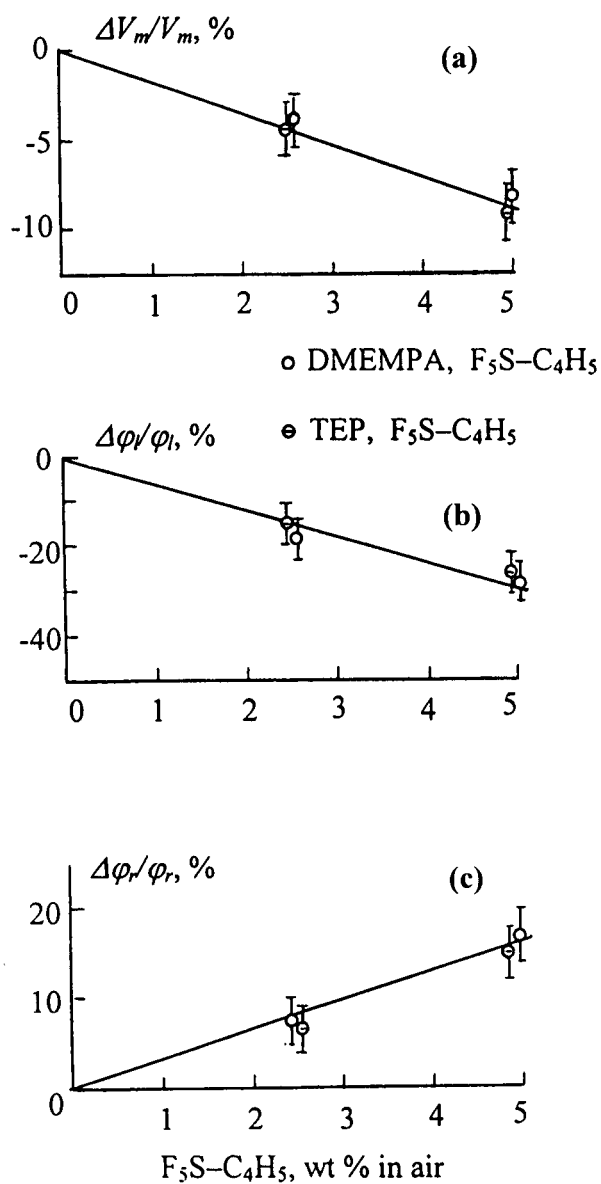


Fig. 2.4.15.

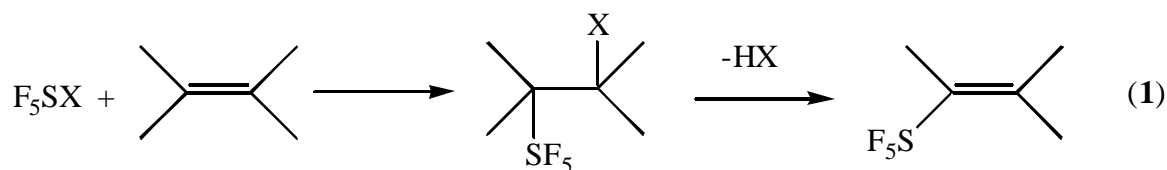
Relative changes in the maximum burning velocities,  $V_m = \max V(\mathbf{j})$  (a), and in the lean,  $\mathbf{j}_l$  (b), and rich,  $\mathbf{j}_r$  (c), concentration flammability limits for various OPEs versus the mass percentage of  $F_5SCH=cycloPr$  in air.

**Table 2.4.1.**

### 3. Synthesis of cyclic and acyclic materials containing the pentafluorosulfanyl group

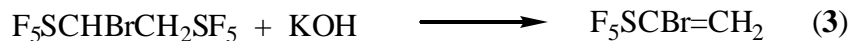
The introduction of pentafluorothio groups ( $\text{SF}_5$ , pentafluoro- $\lambda^6$ -sulfanyl) into molecular systems can bring about substantial changes with regard to their physical, chemical and biological behaviour. These new properties are manifested in a multitude of uses, or potential uses, such as surface-active agents, fumigants, thermally and chemically stable systems, solvents for polymers and perfluorinated blood substitutes [1]. The high thermal and chemical stability of the pentafluorothio group make these compounds attractive as replacements for compounds that contain a trifluoromethyl group. The electronegativity value of the  $\text{SF}_5$ -group appears to be very high; by examining the  $^{13}\text{C}$  NMR chemical shifts of a number of fluorosulfones, a Pauling electronegativity of 3.62 is found [2]. It is, however, comparatively more difficult to introduce this group into a molecule that a  $\text{CF}_3$ -products may be formed [3].

Various methods are at hand to effect such a derivatization, e.g., treatment of disulfides, mercaptans or sulfides with fluorine [4], electrochemical fluorination [5], oxidation of aromatic disulfides with silver (II) fluoride [6],  $\text{SF}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{SF}_5$ ) adds across multiple bonds and forms adducts. Furthermore, tetrafluorosulfur ylides ( $\text{F}_4\text{S}=\text{CR}_1\text{CR}_2$ ) add  $\text{HF}$  to form  $\text{SF}_5$ -compounds; however, as most of these ylides are formed from  $\text{SF}_5$ -compounds, this method is only of limited value [7]. The simple organic derivatives can undergo further reactions; in particular, the primary addition products of  $\text{SF}_5\text{X}$  and alkenes or alkynes can be dehydrohalogenated to yield alkenes or alkynes. Treatment of suitable primary adducts with base results in the formation of the respective alkenes (1) [8].



$\text{X} = \text{Cl}, \text{Br}$ .

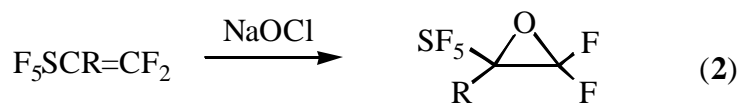
Only in exceptional cases are difficulties encountered ( $\text{HSF}_5$  elimination) (2, 3) [9].



Over 90 different compounds that contain both the  $\text{SF}_5$ -substituent and a double or triple bond were synthesized in the last forty years. These compounds were intended to be versatile building blocks for construction of compounds with  $\text{SF}_5$ -fragment.

The reactions of pentafluorothio olefins are broad, with cycloadditions being rare; 1- $\text{SF}_5$ -1,3-cyclohexadiene can be dehydrogenated to  $\text{C}_6\text{H}_5\text{SF}_5$  [10]. Additions of halogens and pseudohalogens take place easily; nucleophilic and electrophilic additions or nucleophilic substitutions may occur [10,11]. Bromine addition, under the action of light leading to the respective polybromo compounds. Chlorine also adds to  $\text{SF}_5$ -olefins with irradiation.

Nucleophilic additions were observed in several instances:



R = H, F

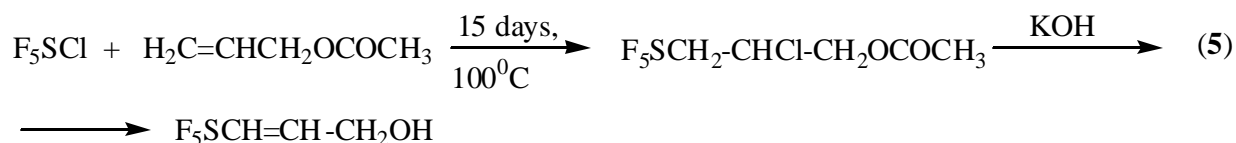
$\text{F}_5\text{SCH}=\text{CHOCH}_3$  can be converted with sodium methoxide in methanol to the dimethyl acetal  $\text{F}_5\text{SCH}_2\text{CH}(\text{OCH}_3)_2$  [10,12]. The same reagent will convert 1-bromo-1- $\text{SF}_5$ -ethylene to  $\text{SF}_5\text{CHBrCH}_2\text{OCH}_3$ .

### 3.1. Results and discussion.

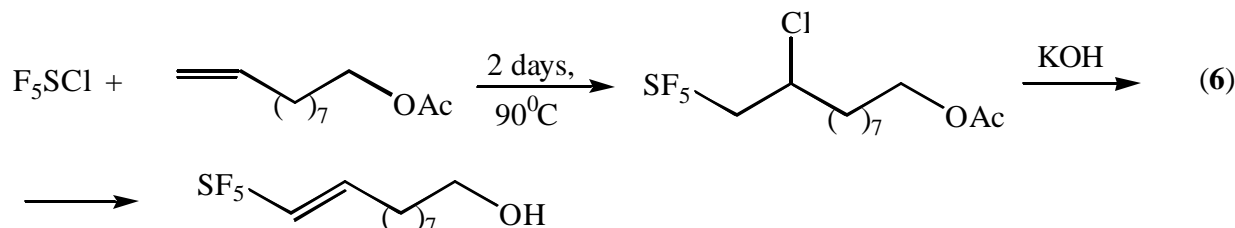
Key stage for preparation of compounds containing the pentafluorosulfanyl group, is the introduction of  $\text{SF}_5$ -groups in organic molecule. The most generally used method for preparing aliphatic derivatives of  $\text{SF}_5$  is to add  $\text{SF}_5\text{Cl}$  to olefin or acetylene under free radical conditions. Both  $\text{SF}_5\text{Cl}$  and  $\text{SF}_5\text{Br}$  react with unsaturated organic compounds. There are numerous examples of the addition of an  $\text{SF}_5$ -group and halogen atom across a  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}\equiv\text{N}$  bond, although under certain conditions fluorination also occurs. The photochemical reactions of  $\text{SF}_5\text{Cl}$  with olefins have been studied in detail and are believed to involve a chain reaction.  $\text{SF}_5\text{Cl}$  behaves as a pseudo-halogen, with  $\text{SF}_5$  as the attacking radical. This is supported by kinetic investigation of the  $\text{SF}_5\text{Cl}/\text{C}_2\text{H}_4$  reaction [13]. The direction of the reaction is guided by the most stable free radical that is first formed between  $\text{SF}_5$  and  $\text{C}=\text{C}$ ; examples are shown in the literature [14]. The regiospecificity of the radical reactions prevails even if a sterically very crowded product is formed. Radical reactions may also be initiated thermally ( $90$ – $100^\circ\text{C}$ ). In this cases some polymerization is observed (in fact, it is found that with isobutene and styrene only polymerization occurs [8a]). With less reactive fluoroolefins, additions of  $\text{SF}_5\text{Cl}$  take place only under photolytic conditions or by using a radical initiator such as benzoyl peroxide.

#### 3.1.1. Interaction of $\text{SF}_5\text{Cl}$ with unsaturated alcohols.

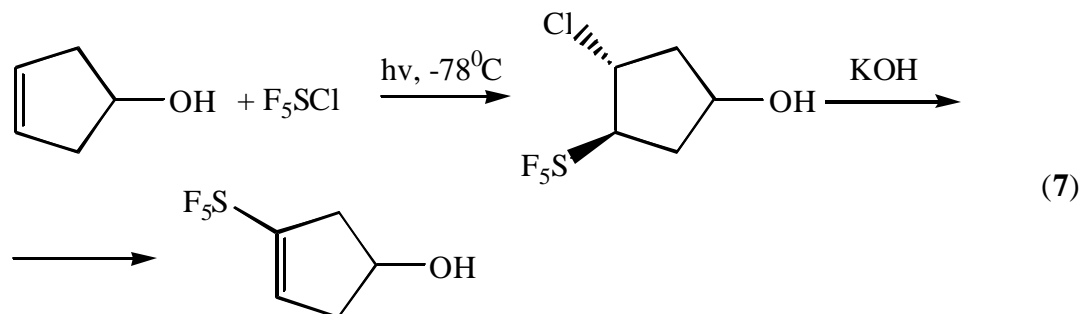
In literature many examples for reactions of  $\text{SF}_5\text{Cl}$  and olefins are presented, however the works on reactions of  $\text{SF}_5\text{Cl}$  and olefins with OH-groups are practically absent. We know only two works, in which was used  $\text{SF}_5\text{Cl}$  for synthesis of unsaturated alcohols with terminal pentafluorothio groups. For example, reaction of addition  $\text{SF}_5\text{Cl}$  to allyl acetate (heating in steel bomb at  $100^\circ\text{C}$  for 15 days) with subsequent elimination of  $\text{HCl}$  from 2-chloro-3- $\text{SF}_5$ -propyl acetate lead to allylic alcohol [1f].



The 10- $\text{SF}_5$ -9-Decen-1-ol was synthesized in two step from 9-decenyl-1-acetate and  $\text{SF}_5\text{Cl}$  (heating in steel bomb at  $90^\circ\text{C}$  for 2 days) [15].

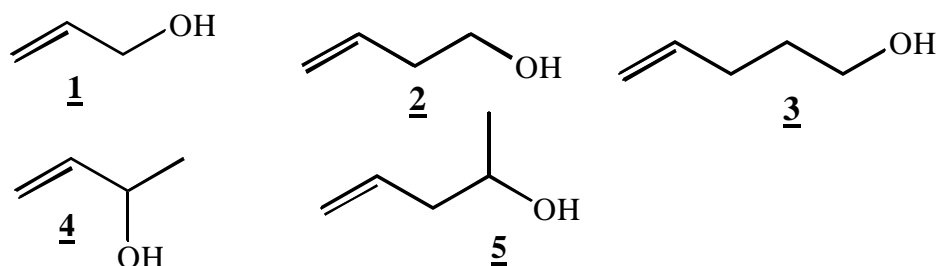


A recent report from Seppelt's laboratory described a photochemical addition of  $\text{SF}_5\text{Cl}$  to cyclic unsaturated alcohols [16].

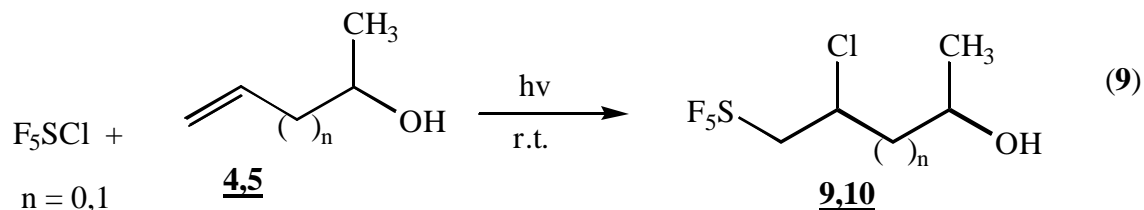
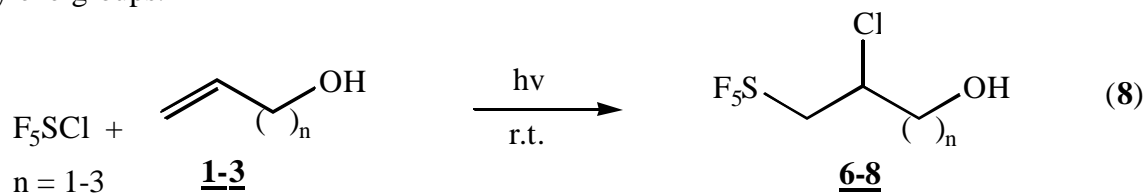


In continuation of earlier begun works we have tried to compare two approaches to introduction of  $\text{SF}_5$ -groups in unsaturated alcohols: photochemical and thermal.

In quality of objects research, we used unsaturated alcohols with terminal position of double bonds 1-5.



We used photochemical and thermal reactions for introduction of pentafluorosulfanyl ( $\text{SF}_5$ ) group into compounds 1-5. Photochemical reactions was realized in glass (Pyrex) ampoule. Irradiation (quartz mercury lamp) of unsaturated compounds 1-5 and pentafluorothio chloride in trifluorochloromethane led to adducts 6-10. The yields after distillation were  $> 80\%$ . The direction of the photochemical addition is regiospecific,  $\text{F}_5\text{S}$ -radical adds only to terminal methylene groups.



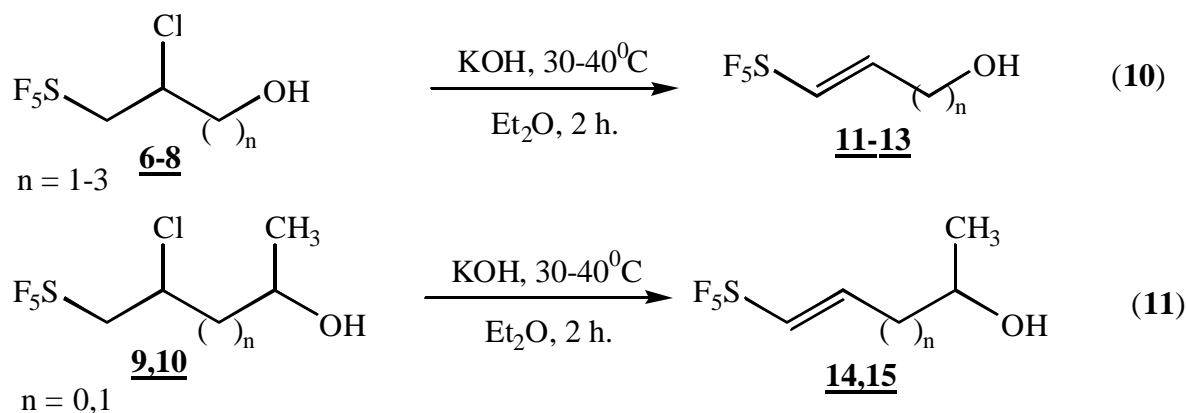
The reactions of addition  $\text{SF}_5\text{Cl}$  were also carried out at pressure in a stainless-steel bomb. Addition of  $\text{SF}_5\text{Cl}$  to a double bond in this case was possible, but adducts 6-10 were prepared only with 20-27% yields. The products thus obtained were identical with the corresponding products prepared by photochemical reactions. Adducts 6-10 were stable and could be isolated by distillation in vacuum (Table 1). The alcohols 9-10 were obtained as mixtures of two diastereomers ( $^{19}\text{F}$  NMR spectral data, in 1:0.8 ratio).

Table 1.

Compounds	Bp °C/mm Hg	Photochemical reaction Yield, %	Autoclave reaction Yield, %
<b>6</b>	68/3	83	20
<b>7</b>	92/5	80	23
<b>8</b>	102/2	84	27
<b>9</b>	93/12	83	21
<b>10</b>	98/5	85	23

Compounds **6-10** were identified by IR,  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. The infrared spectra for all new compounds have in common the characteristic absorption bands of the  $\text{SF}_5$  group. Cross and coworkers reported that the most intense band for compounds containing the  $\text{SF}_5$  grouping should appear in the region  $850\text{-}920\text{ cm}^{-1}$  (S-F stretching modes) and in the region of  $600\text{ cm}^{-1}$  (S-F deformation modes) [17]. For the compounds **6-10**, the stretching absorption bands are found in the  $815\text{-}890$  region while the deformation band is located in the  $580\text{-}600\text{ cm}^{-1}$  region. The compounds **6-10**, show a typical  $\text{AB}_4$  splitting pattern in the  $^{19}\text{F}$  NMR spectrum for the  $\text{SF}_5$ -group. The axial fluorine (A) appears as a distorted pentet (or nine-line pattern) in the range of  $159\text{-}162\text{ ppm}$ , and the equatorial fluorine (B) as a doublet of multiplets in the range of  $144\text{-}145\text{ ppm}$ ,  $J_{\text{AB}} = 148\text{-}159\text{ ppm}$ . Compounds **9-10** have chemical shifts and coupling constants for the fluorines  $\text{SF}_5$  group in good agreement with other pentafluoro- $\lambda^6$ -sulfanyl derivatives [16,18]. The  $^1\text{H}$  NMR spectrum of the compounds **6-10** contained signals of the protons for  $\text{CH}_2\text{-SF}_5$  groups at  $4.1\text{ ppm}$  and the signals at  $3.9$  and  $4.5\text{ ppm}$  related to the protons at  $\text{CH}_2\text{OH}$  and  $\text{CHCl}$ . The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of some compounds are shown on Figure 1-6.

Compounds **6-10** are stable compounds, but under basic conditions they are easy elimination of  $\text{HCl}$ . The olefins **11-15** containing  $\text{SF}_5$  group were synthesized by 1,2-elimination of hydrogen chloride from chloroalkanes **6-10** by means of potassium hydroxide in the dry inert solvent (diethyl ether or tetrahydrofuran) at  $30\text{-}40^\circ\text{C}$  for 2 h. Reactions were monitored by TLC on  $\text{SiO}_2$  and  $^{19}\text{F}$  NMR spectral data. Compounds **11-15** were isolated as stable, colorless liquid by distillation. All olefins containing  $\text{SF}_5$  group are mixture *cis*- and *trans*-isomers in  $\approx 20\text{:}1$  ratio as indicated by  $^1\text{H}$  NMR.

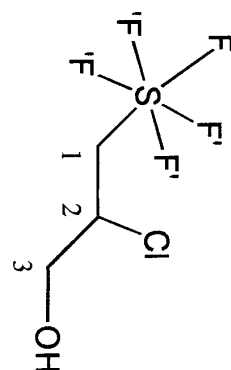


Compounds **11-15** were identified by IR,  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of some compounds are shown on Figures 7-15.

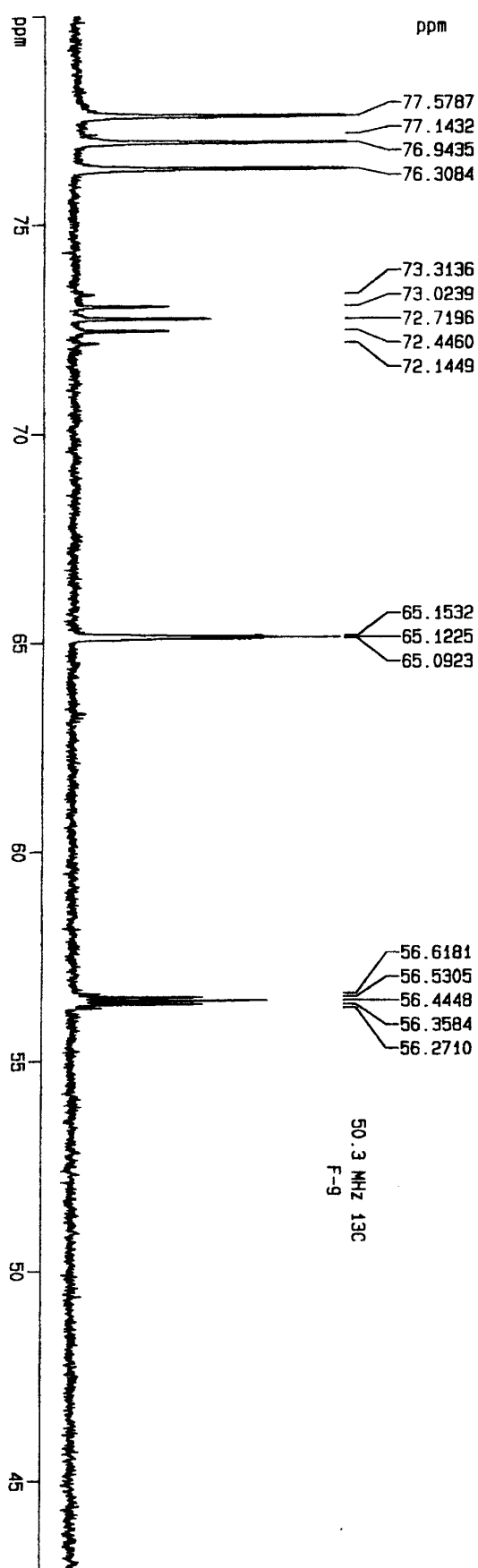
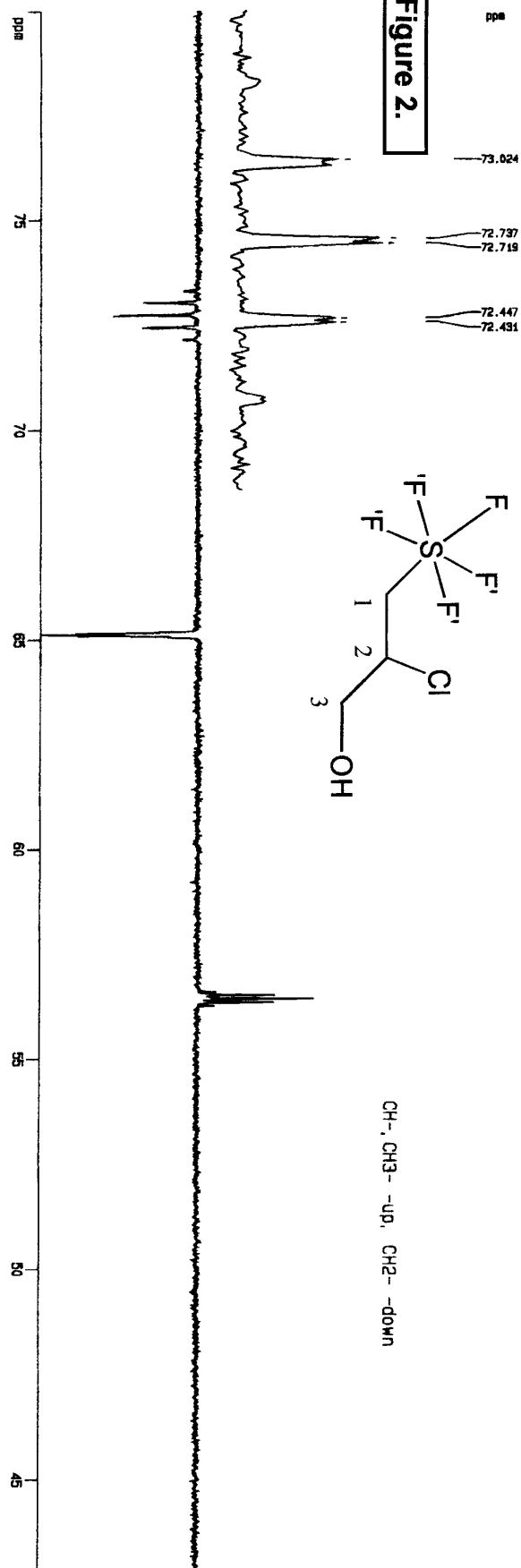
**Figure 1.**



Figure 2.

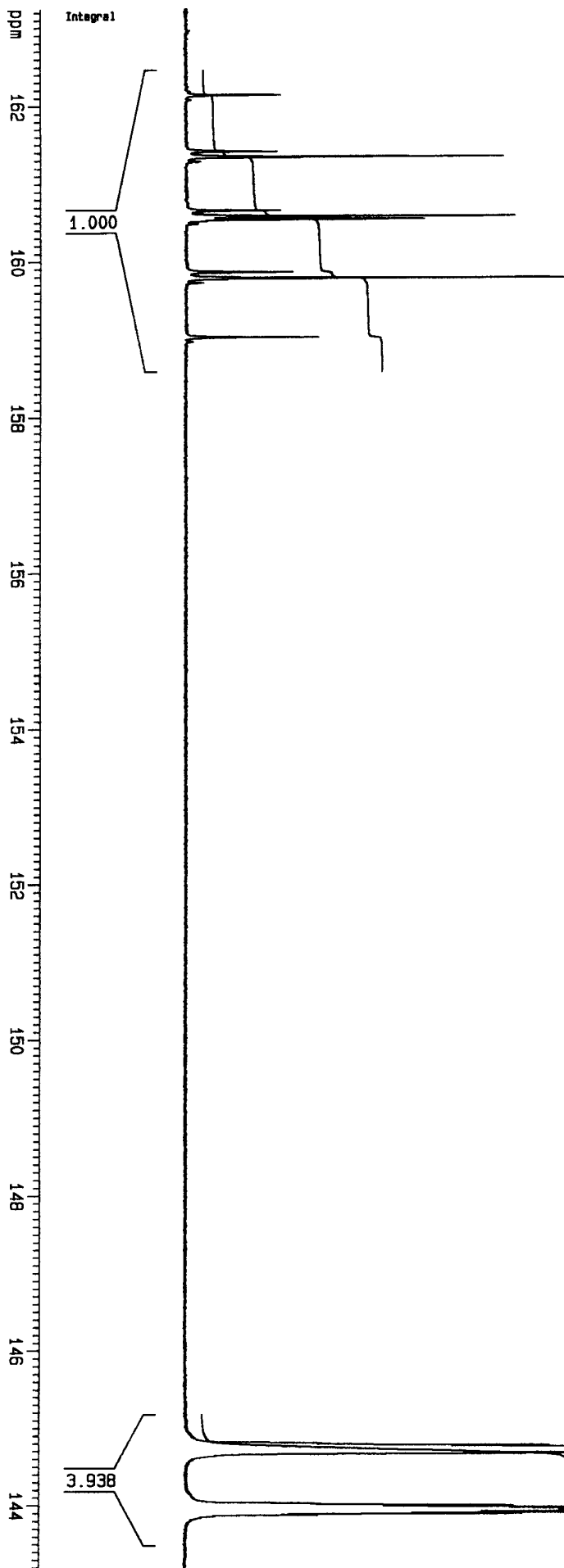
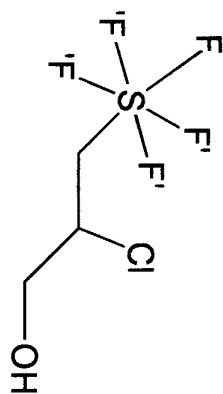


CH-, CH<sub>3</sub>- --up, CH<sub>2</sub>- --down



188.31 MHz  $^{19}\text{F}$   
F-9 ( $\text{CDCl}_3$ ), ref.  $\text{CF}_3\text{COOH}$

**Figure 3.**



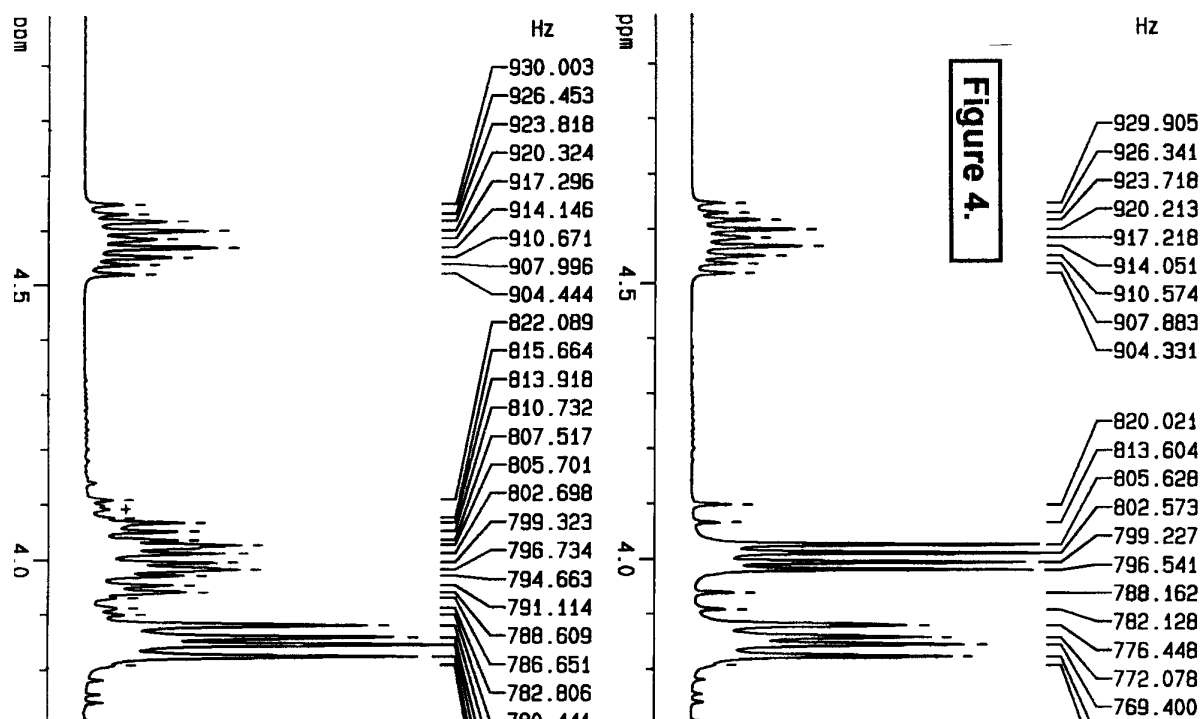
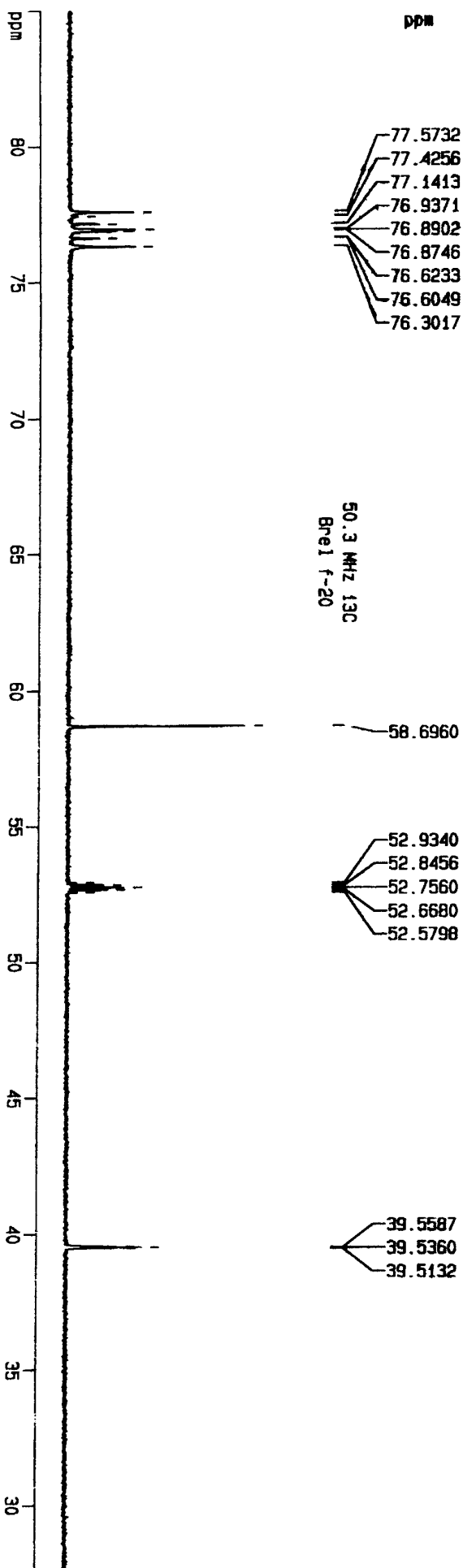
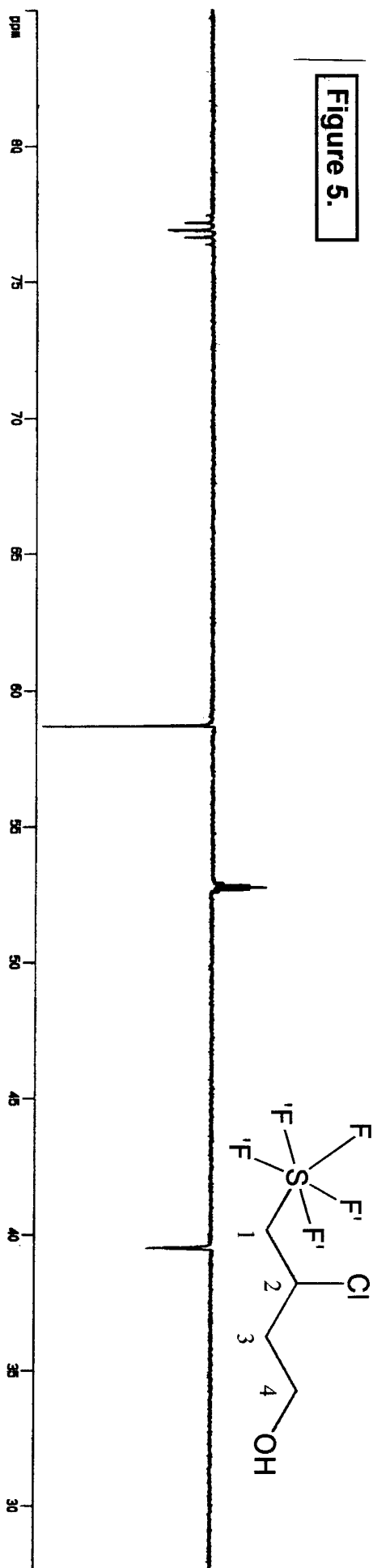
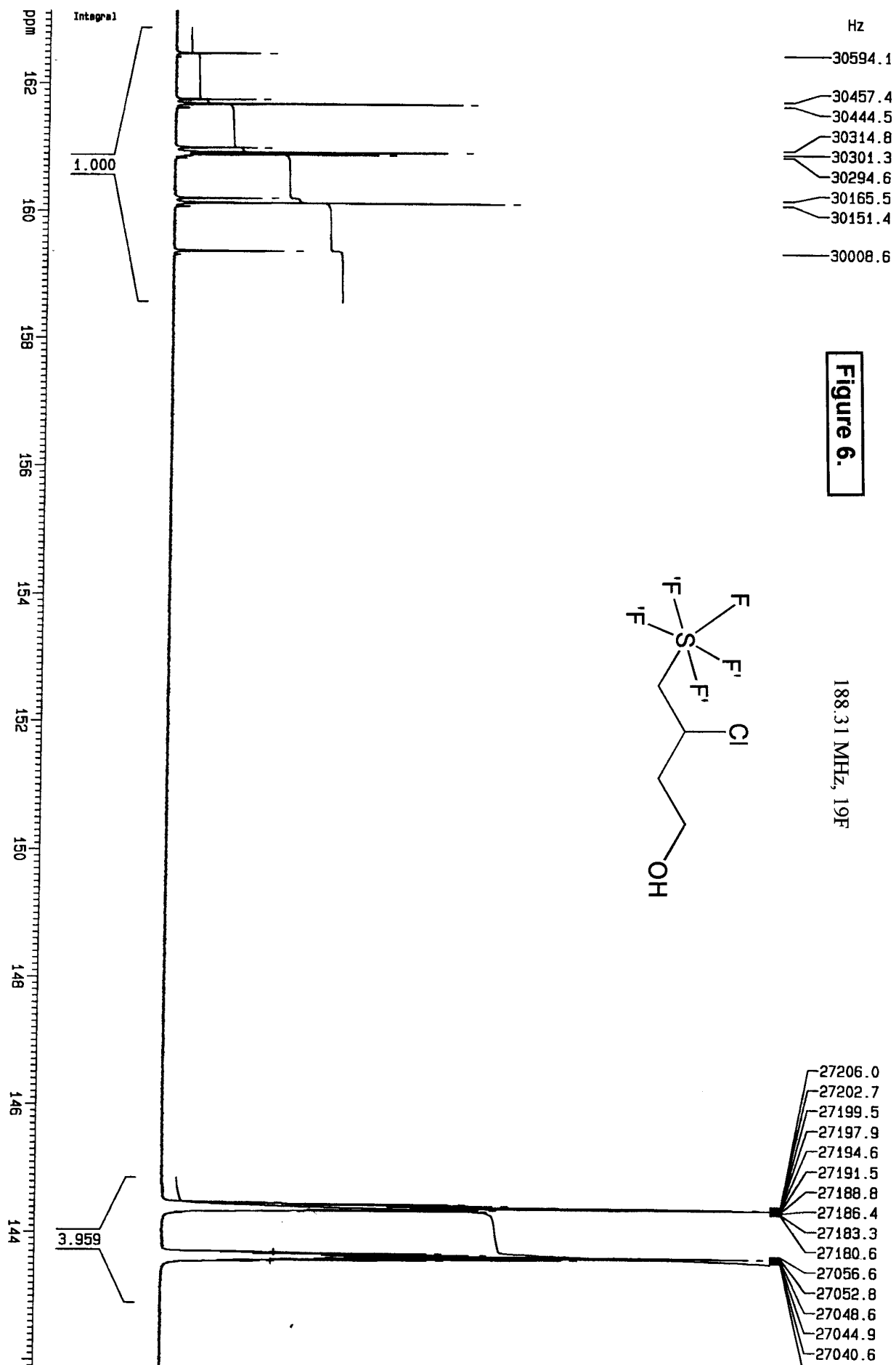
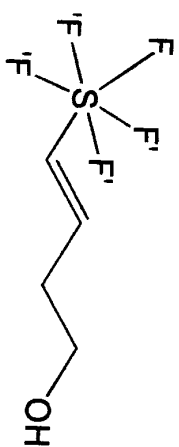


Figure 5.





**Figure 7.**200.13 MHz,  $^1\text{H}$  { $^{19}\text{F}$ }200.13 MHz,  $^1\text{H}$  { $^{19}\text{F}$ }

F-26

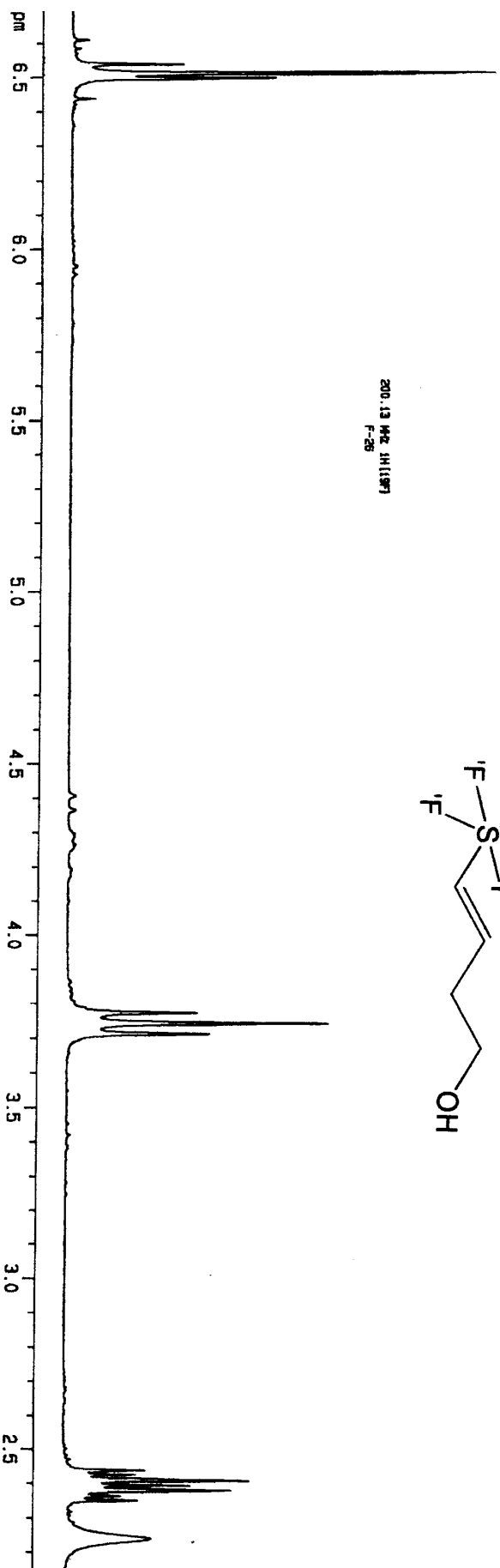
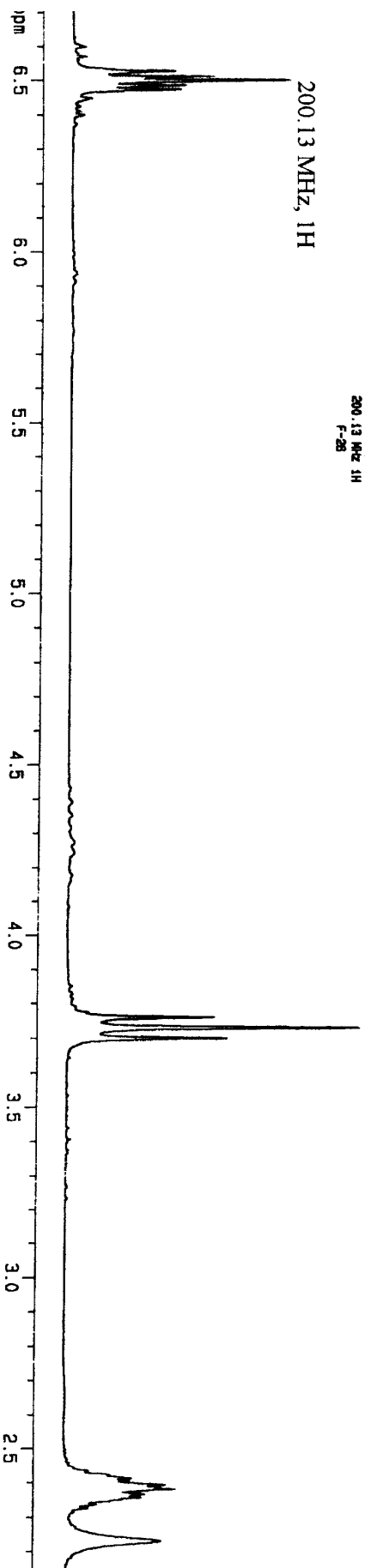
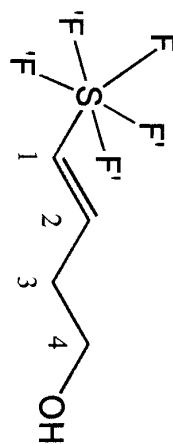
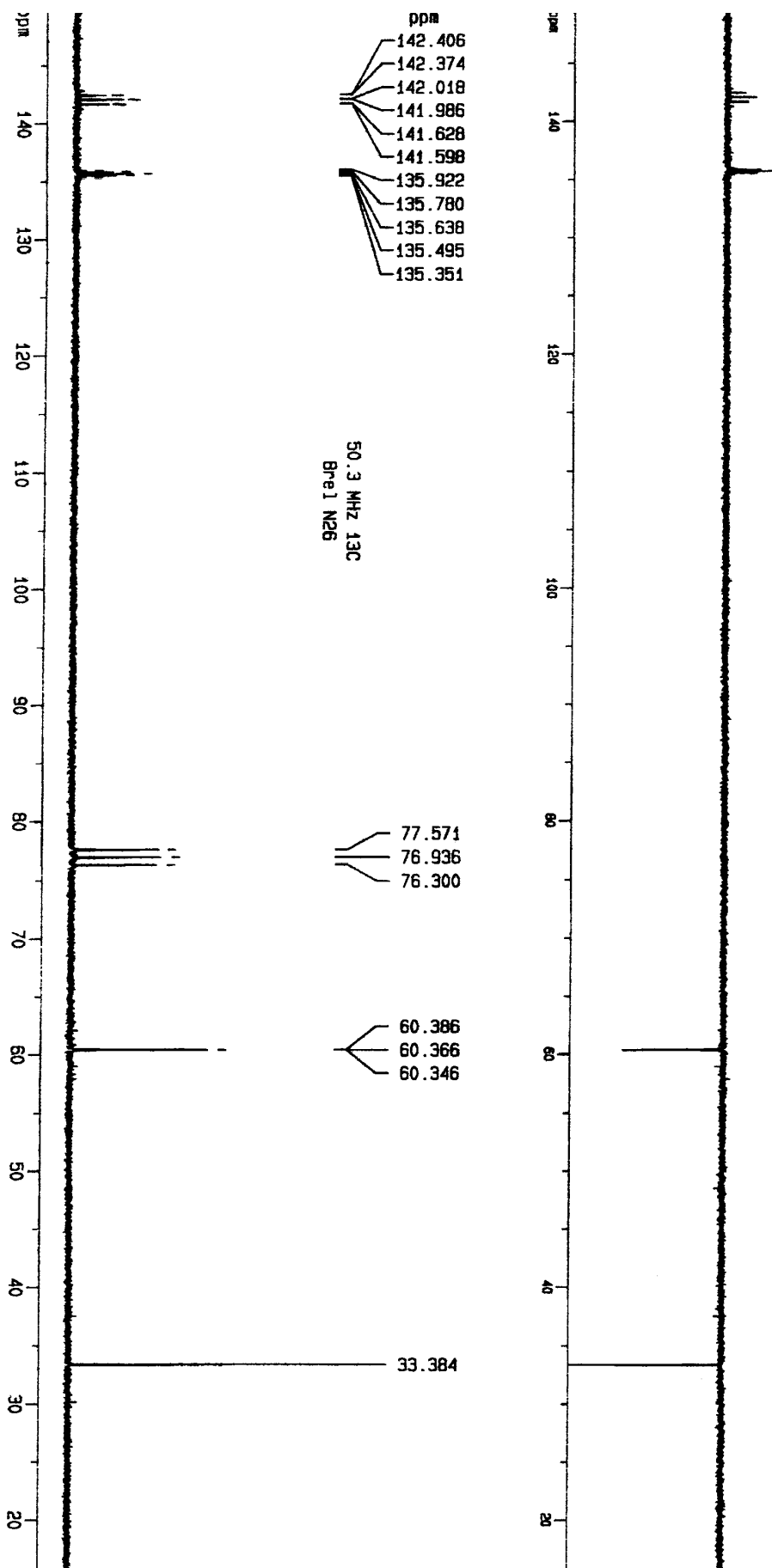
200.13 MHz,  $^1\text{H}$ 200.13 MHz  $^1\text{H}$   
F-26

Figure 8.



CH-, CH3- -up, CH2- -down

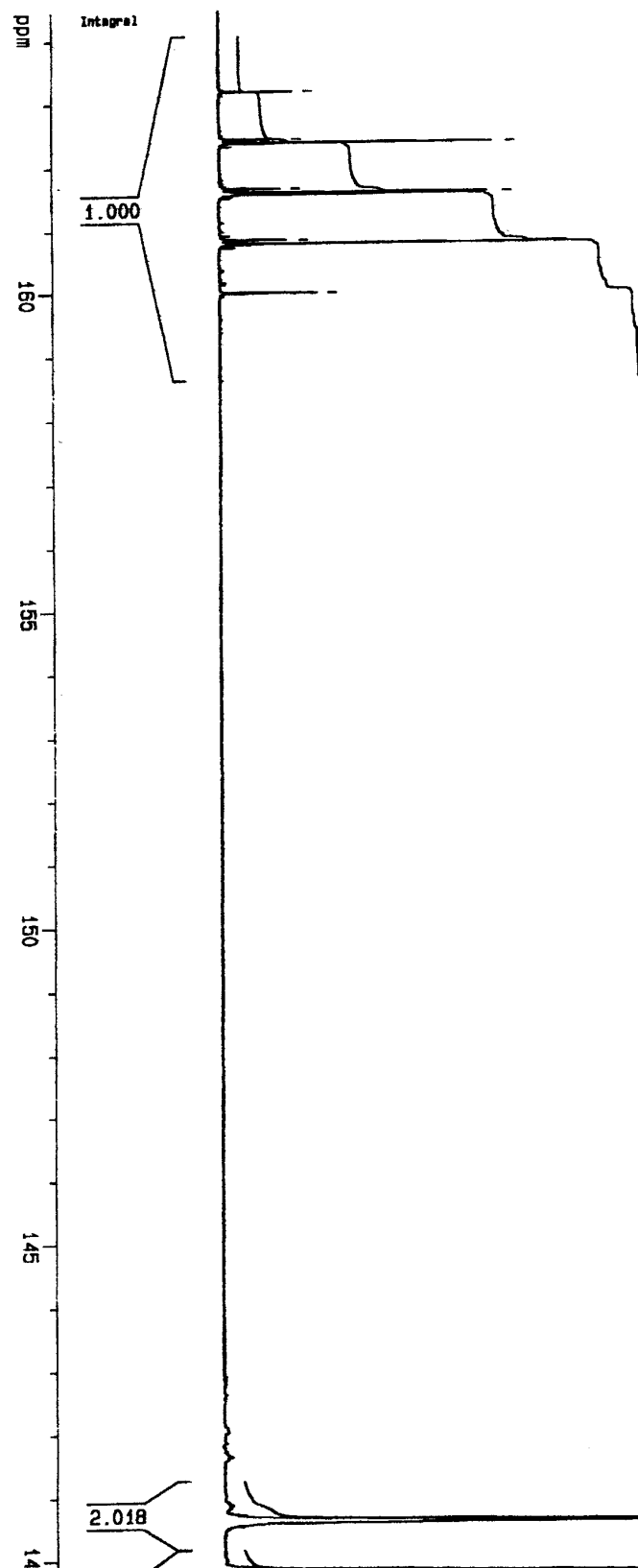
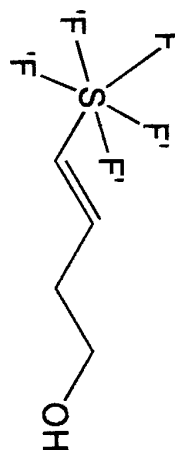


Hz

30725.4  
30583.5  
30572.6  
30436.5  
30425.3  
30419.7  
30284.0  
30272.3  
30125.2

**Figure 9.**

188.31 MHz, 19F

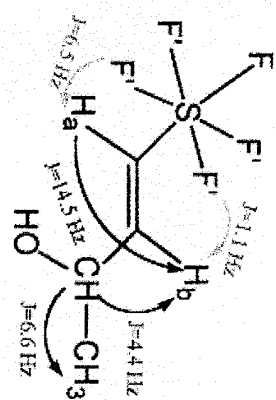


26485.1  
26483.1  
26480.8  
26478.5  
26476.4  
26474.1  
26335.9

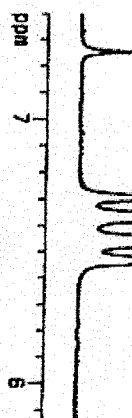


200.13 MHz  $^1\text{H}$  {F}

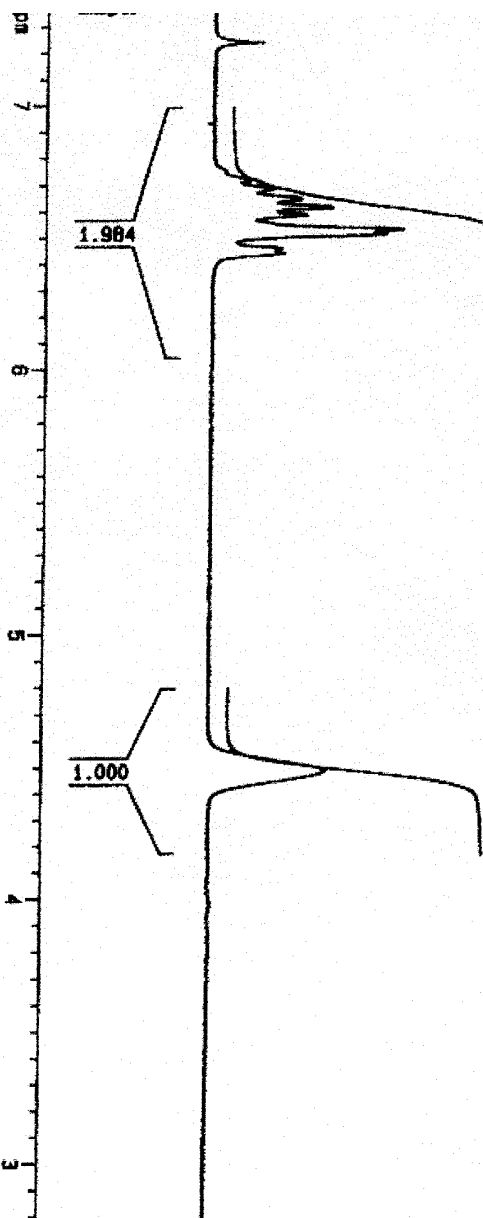
Figure 10.



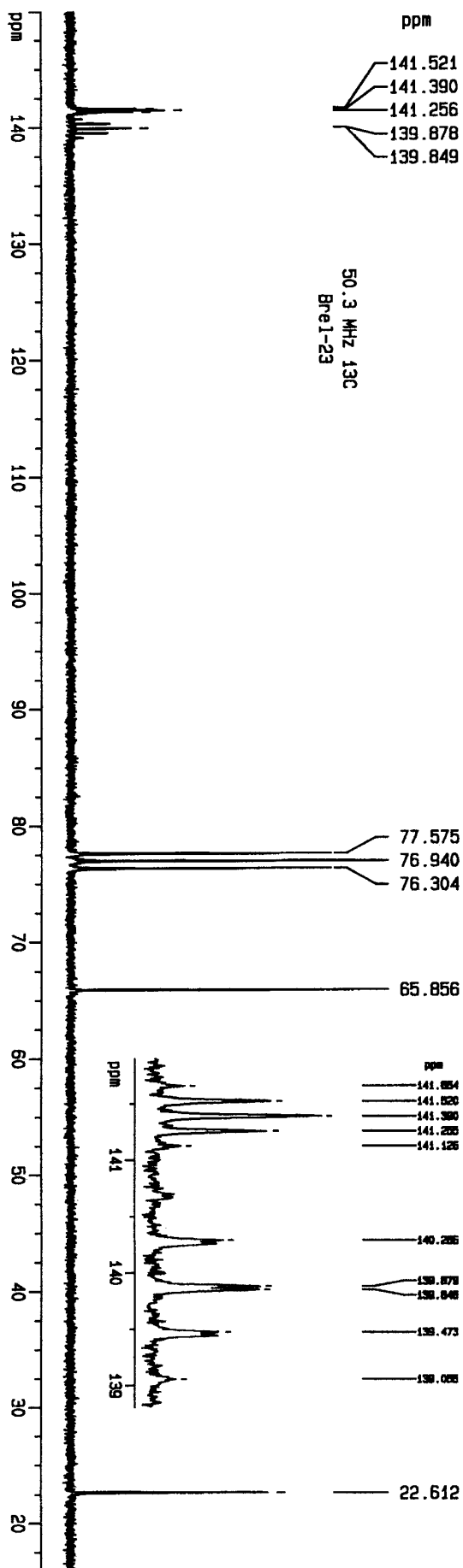
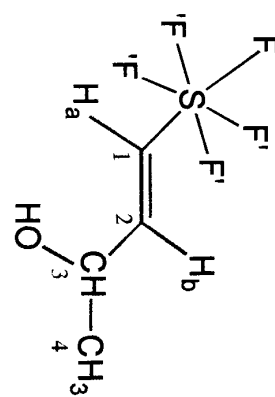
$\delta \text{H}_a =$   
 $\delta \text{H}_c =$   
 $\delta \text{CH}_3$



200.13 MHz  $^1\text{H}$



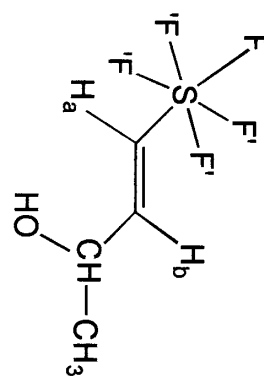
CH-, CH3- -up, CH2- -down

**Figure 11.**

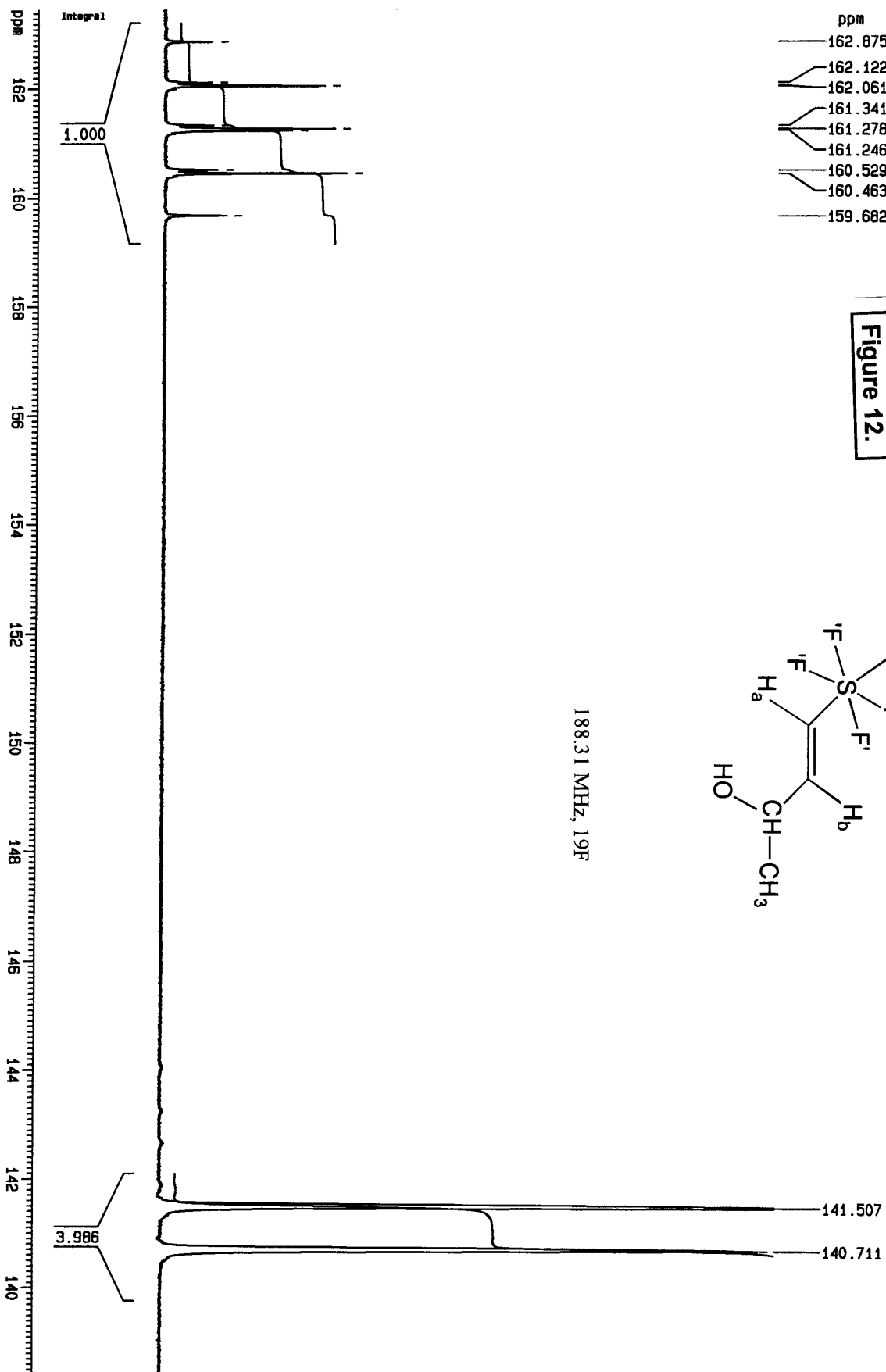
19F Bre1-23

ppm  
162.875  
162.122  
162.061  
161.341  
161.278  
161.246  
160.529  
160.463  
159.682

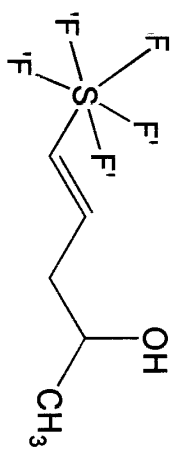
Figure 12.



188.31 MHz, 19F

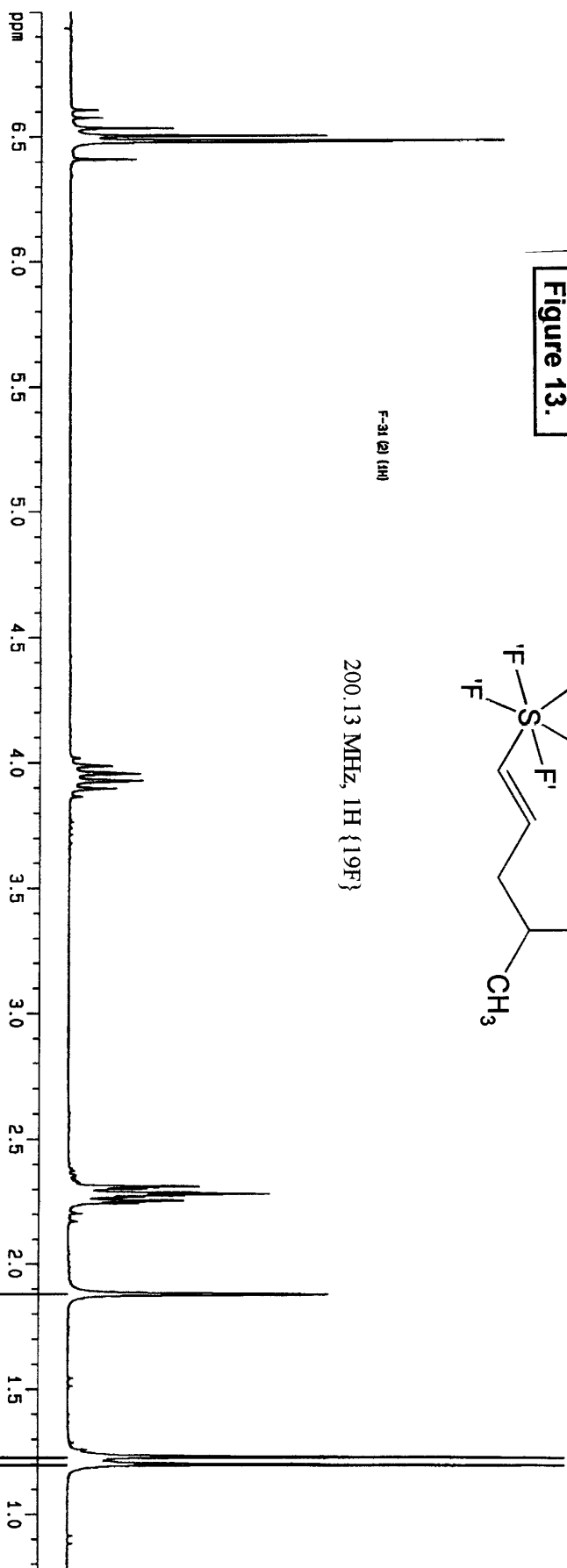


**Figure 13.**



F-31 (2) (1H)

200.13 MHz, 1H {19F}



F-31 (2)

200.13 MHz, 1H

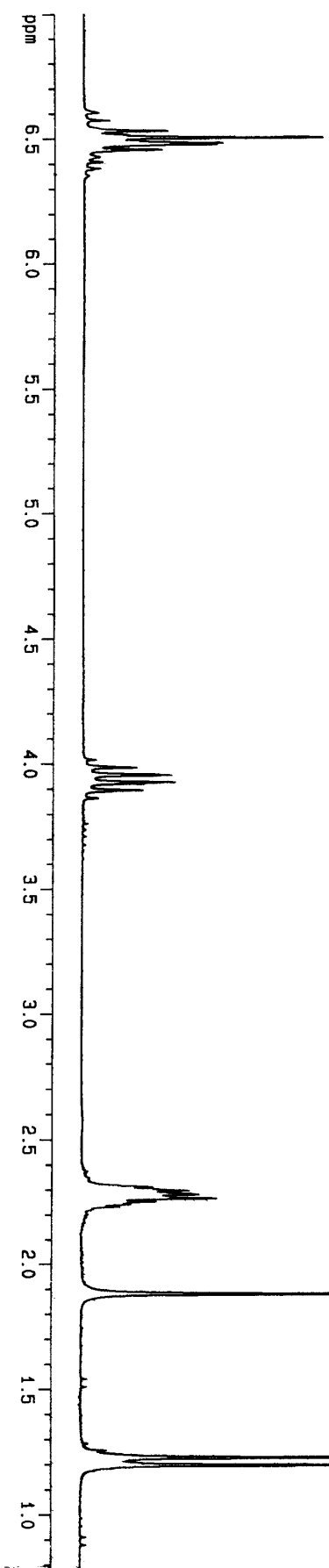
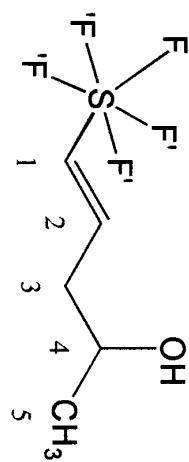
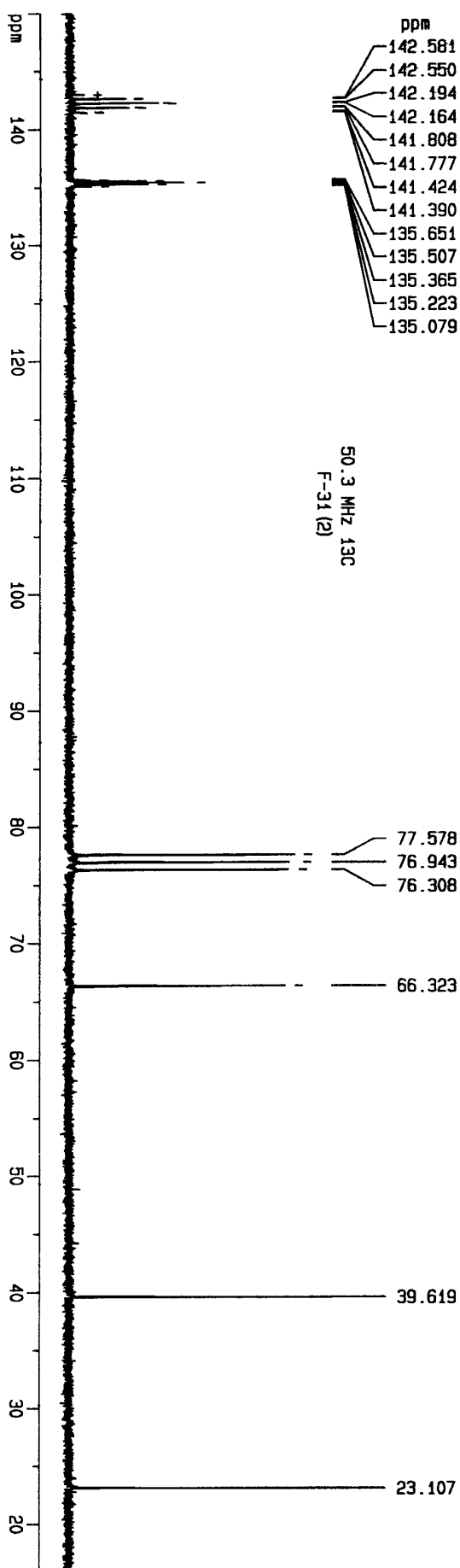
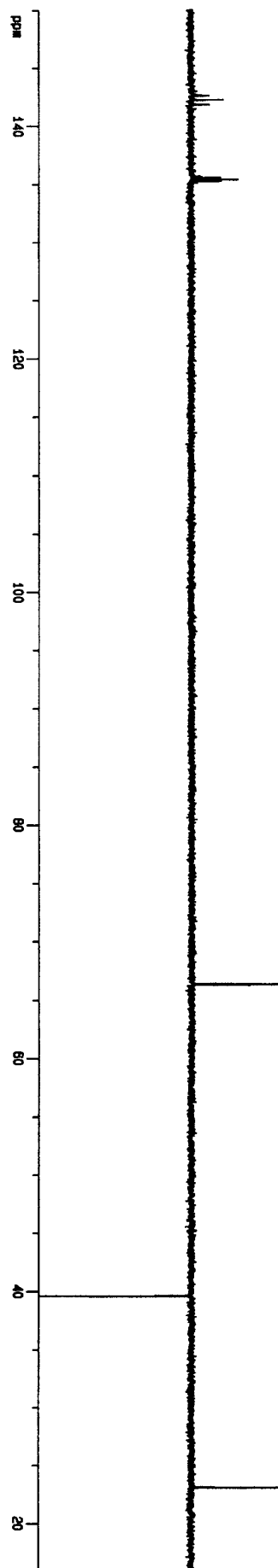
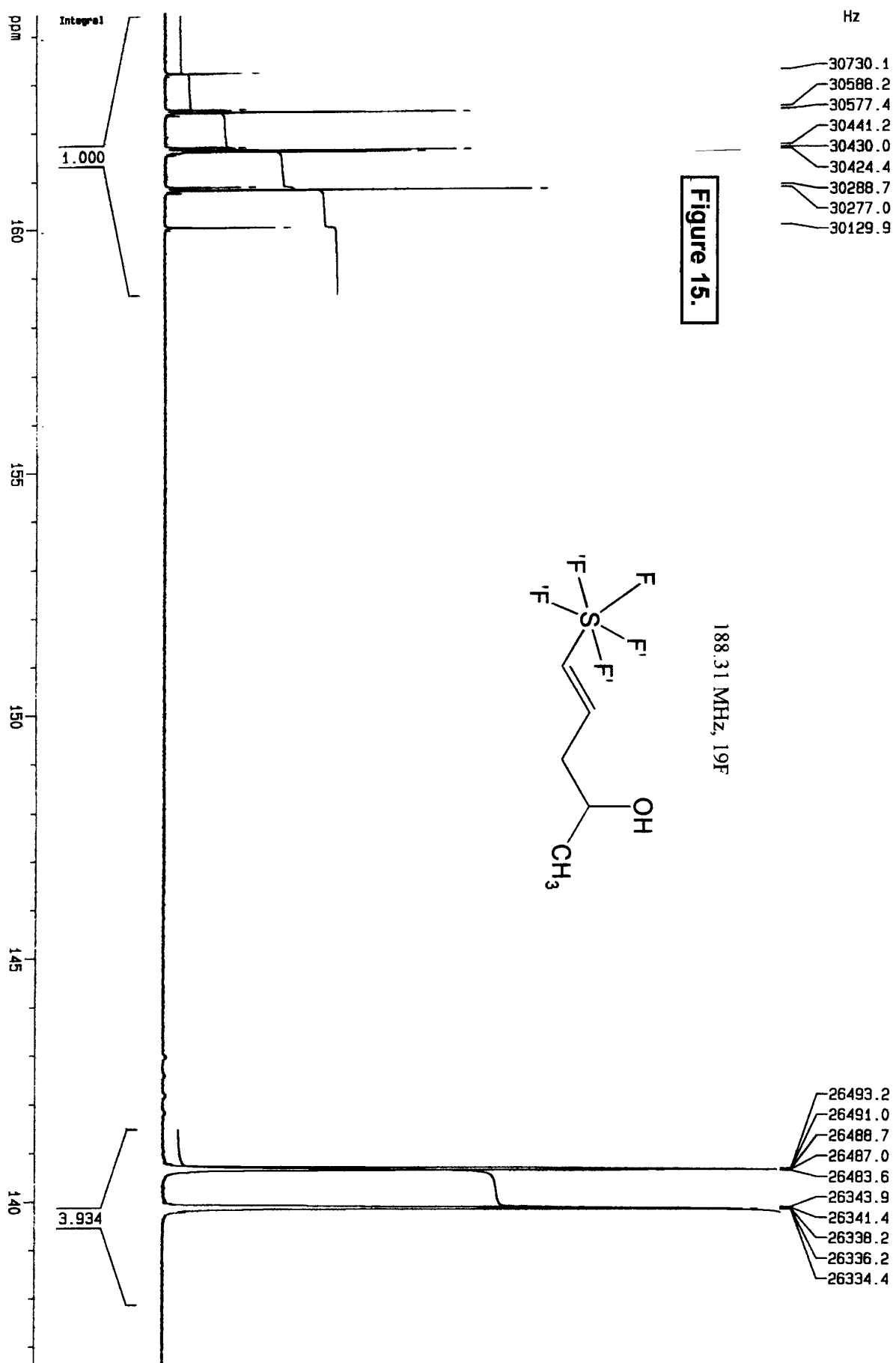


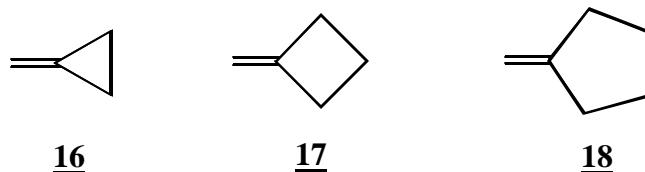
Figure 14.

CH-, CH<sub>3</sub>- -up, CH<sub>2</sub>- -down



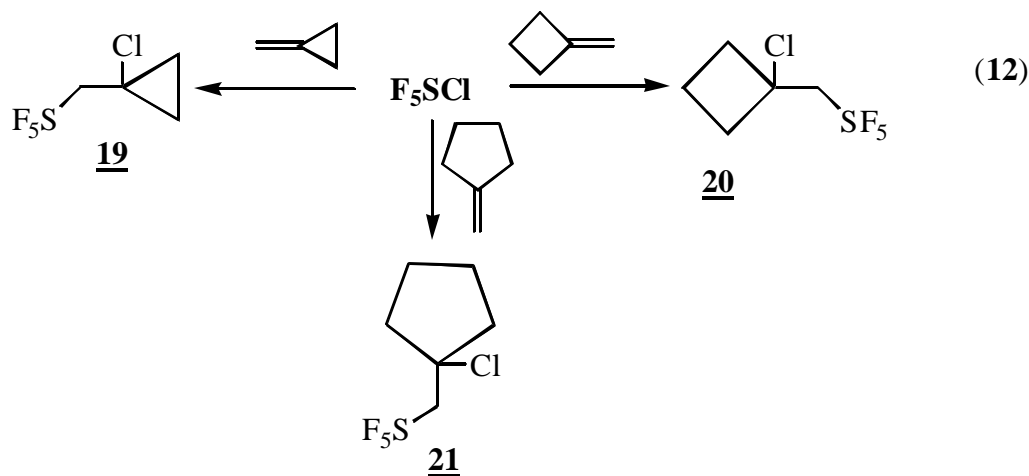
### 3.1.2. Interaction of SF<sub>5</sub>Cl with unsaturated cyclic compounds.

On the next step our research was study of interaction of SF<sub>5</sub>Cl with unsaturated cyclic compounds. In quality of objects research, we used unsaturated cyclic compounds with terminal position of double bonds **16-18**.



Interaction SF<sub>5</sub>Cl with cyclic compounds, which have double bond in terminal position were not studied earlier and the compounds this type were not synthesized.

As well as with unsaturated alcohols, reaction with compounds **16-18** have carried out at a ultra-violet irradiation (photochemical reaction), and also thermal, at heating in stainless steel reaction vessel.



Photochemical reactions were realized in glass (Pyrex) ampoule. Irradiation (quartz mercury lamp) of unsaturated compounds **16-18** and pentafluorothio chloride in trifluorochloromethane led to adducts **19-21**. The direction of the photochemical addition is regiospecific, F<sub>5</sub>S-radical adds only to terminal methylene groups. Adducts **19-21** were stable and could be isolated by distillation in vacuo. The yields after distillation were > 90%. The <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra of some compounds are shown on figures **16-20**.

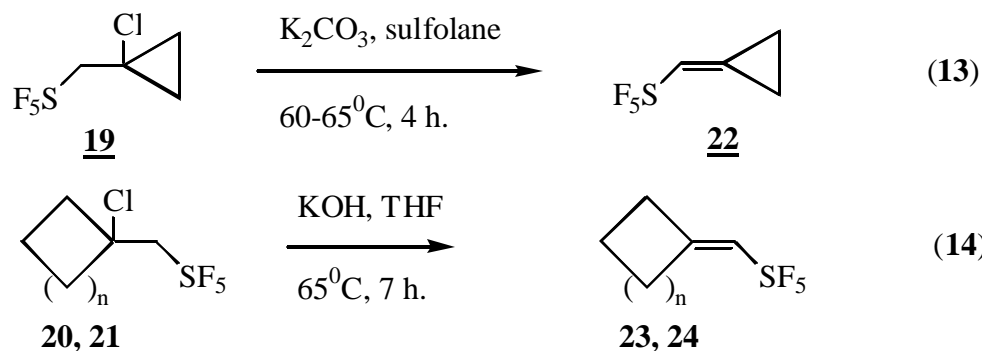
The reactions of addition SF<sub>5</sub>Cl to cyclic compounds containing internal double bonds were also carried out at pressure in a stainless-steel bomb. Addition of SF<sub>5</sub>Cl to a double bond in this case was possible, and adducts **19-21** were prepared with 75-80% yields (Table 2). The products thus obtained were identical with the corresponding products prepared by photochemical reactions.

Table 2

Compounds	Bp °C/mm Hg	Photochemical reaction Yield, %	Autoclave reaction Yield, %
<b>19</b>	60/25	94	75
<b>20</b>	57/15	91	80
<b>21</b>	66/15	93	76

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of some compounds are shown on Figure 0-00.

Using reaction of elimination of hydrogen chlorine from compounds **19-21** by means of potassium hydroxide in the diethyl ether (or in the tetrahydrofuran) or potassium carbonate in the tetramethylene sulfone we synthesized new unsaturated cyclic compounds with pentafluorosulfanyl ( $\text{SF}_5$ ) group.



The progress of the reaction was monitored by the disappearance of signals of the terminal  $\text{F}_5\text{SCH}_2$  of the starting compounds **19-21** in the  $^1\text{H}$  NMR spectra and by the appearance of signal corresponding to the resonance of the protons of the  $\text{F}_5\text{SCH=}$  group in the compounds **22-24**. Compounds **22-24** were isolated as stable, colorless liquid by distillation and identified by IR,  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. The  $^1\text{H}$  NMR spectrum of the compounds **22-24** contained signals of the protons for  $\text{F}_5\text{SCH=}$  group at 6.2 – 6.8 ppm and for protons of a cycle. The chemical shift of fluorine for **22-24** was characteristic for derivatives with pentafluorosulfanyl group, typical  $\text{AB}_4$  system. The low-field position for the two carbon atom (near 130-152 ppm relative to tetramethylsilane) allows the easily identification of the double bound by  $^{13}\text{C}$  NMR spectroscopy. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of compounds **22,23** are shown on Figures 21-25.





Figure 16.

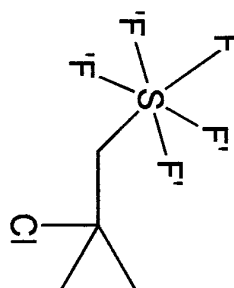
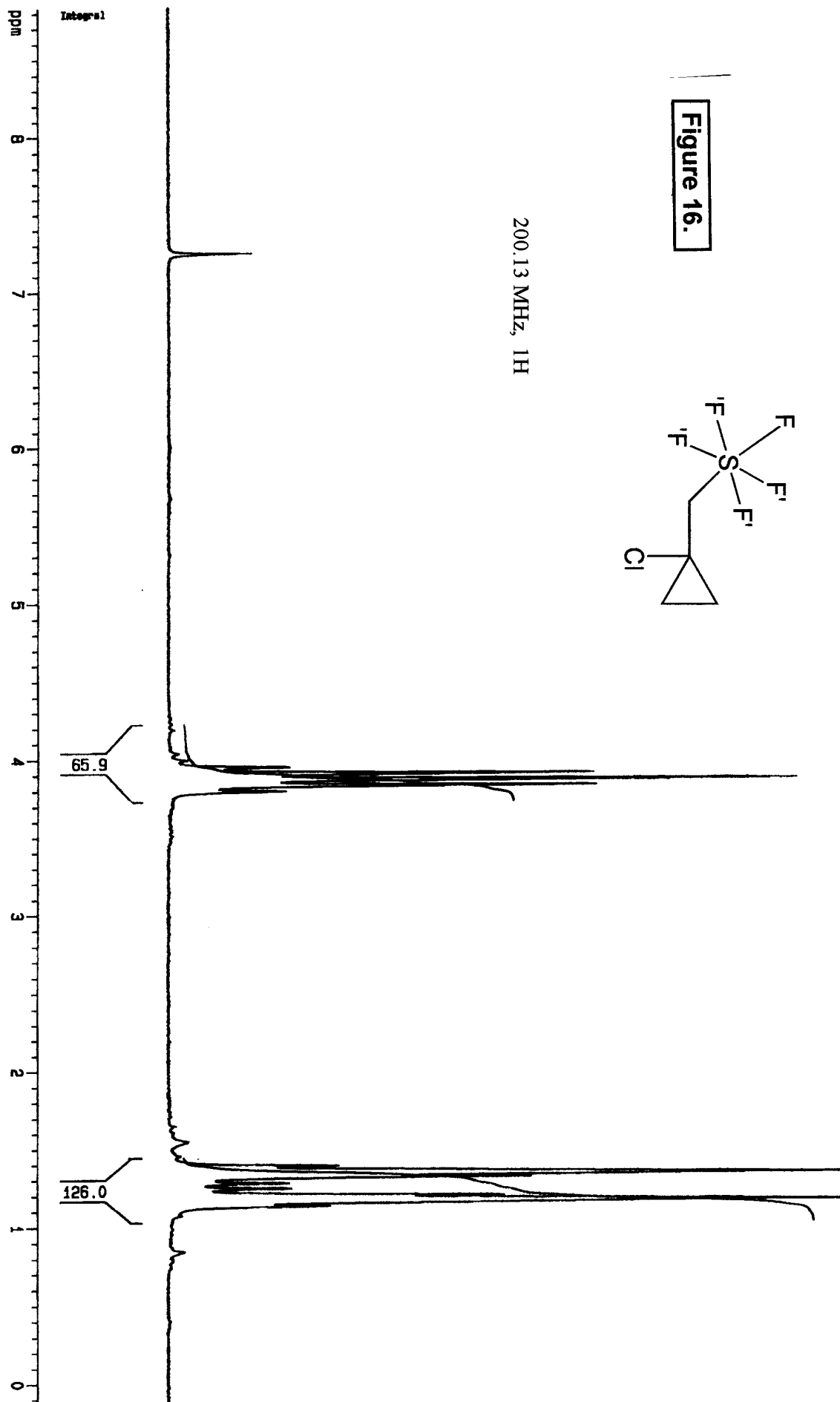
200.13 MHz, <sup>1</sup>H

Figure 17.

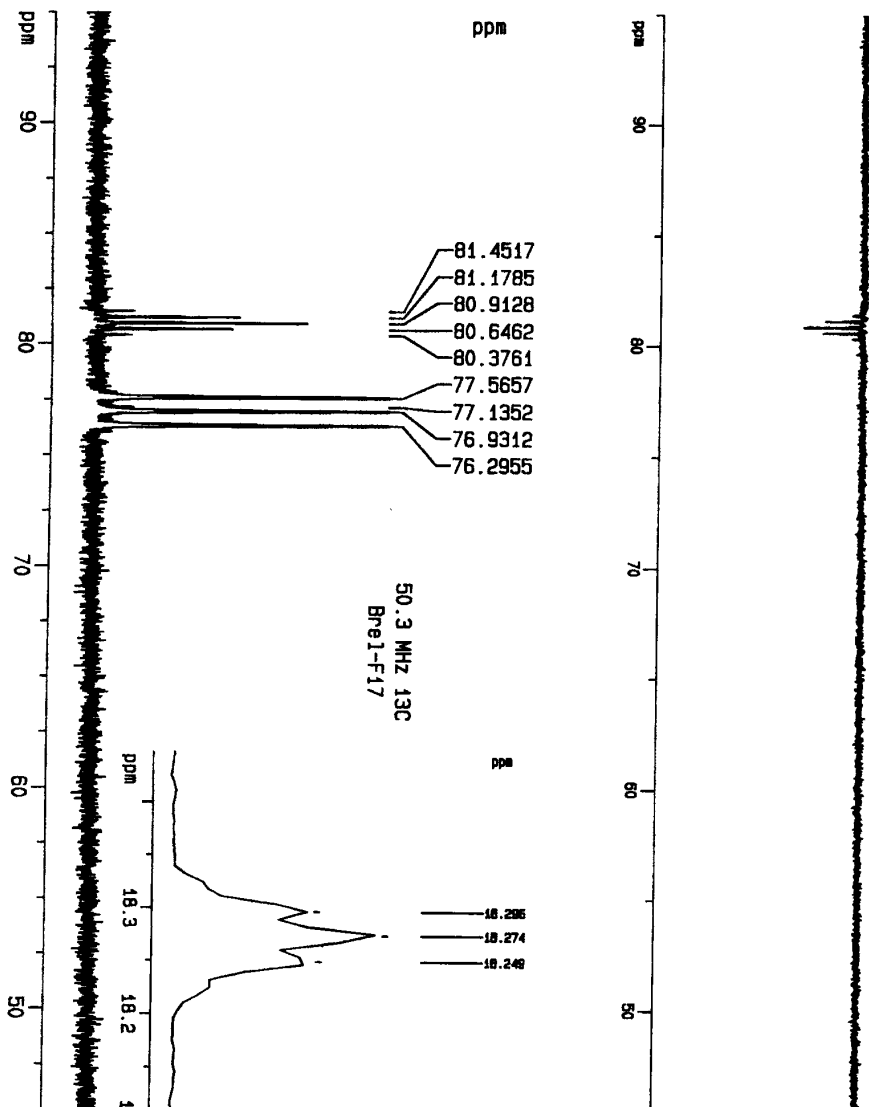
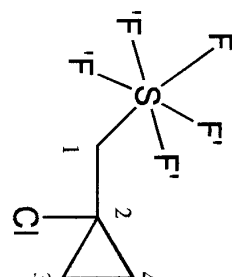
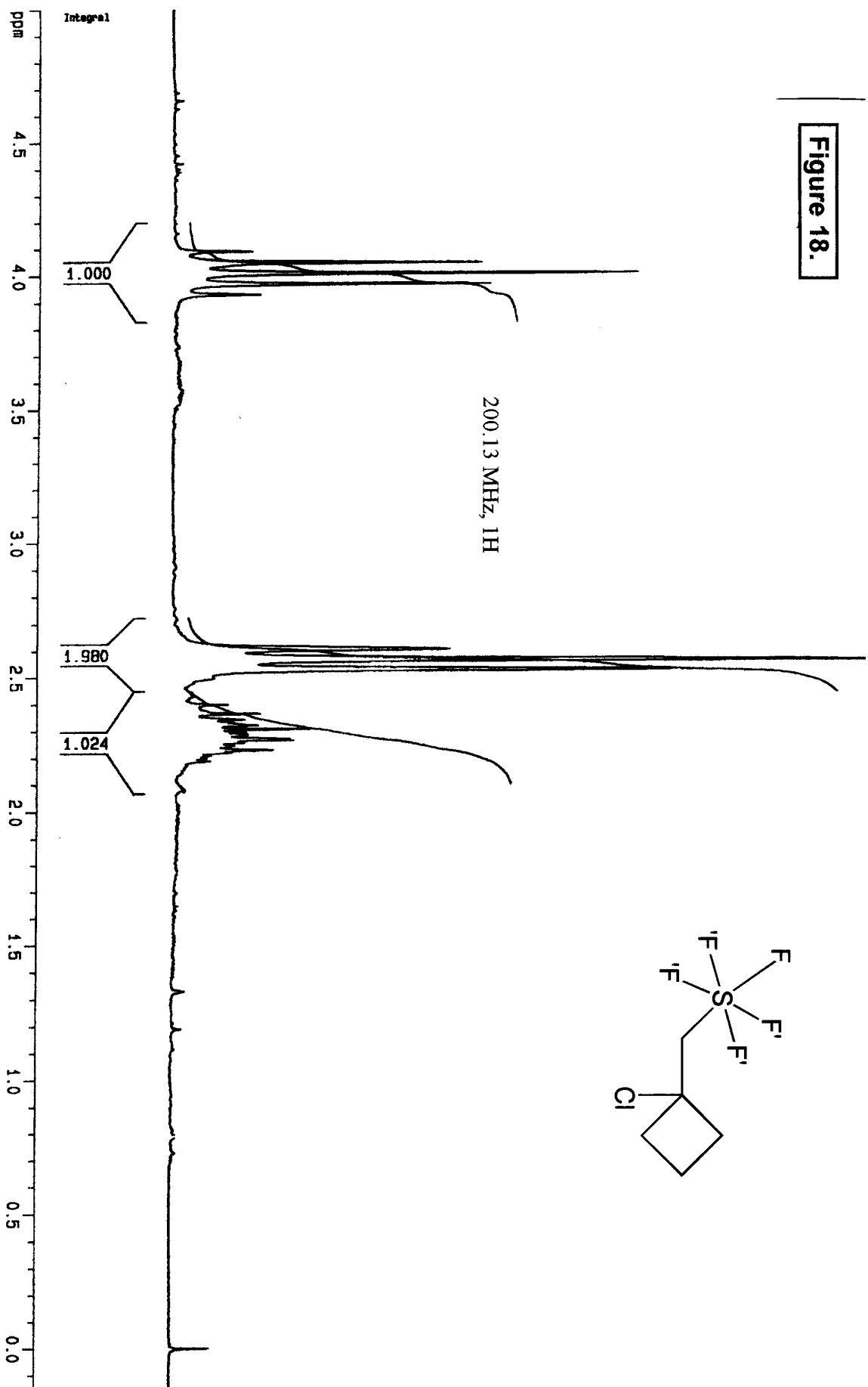


Figure 18.



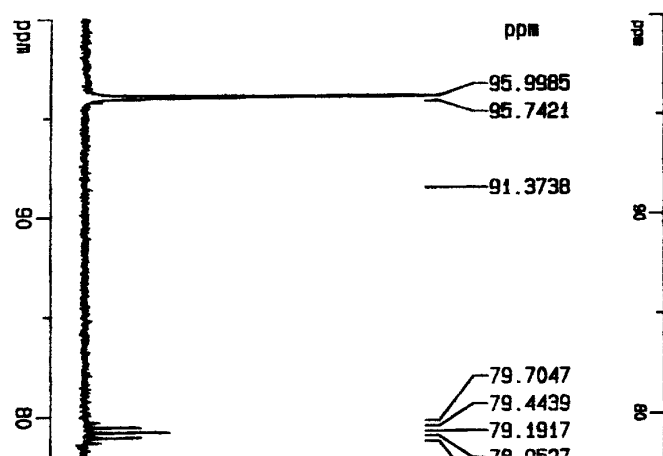


Figure 19.

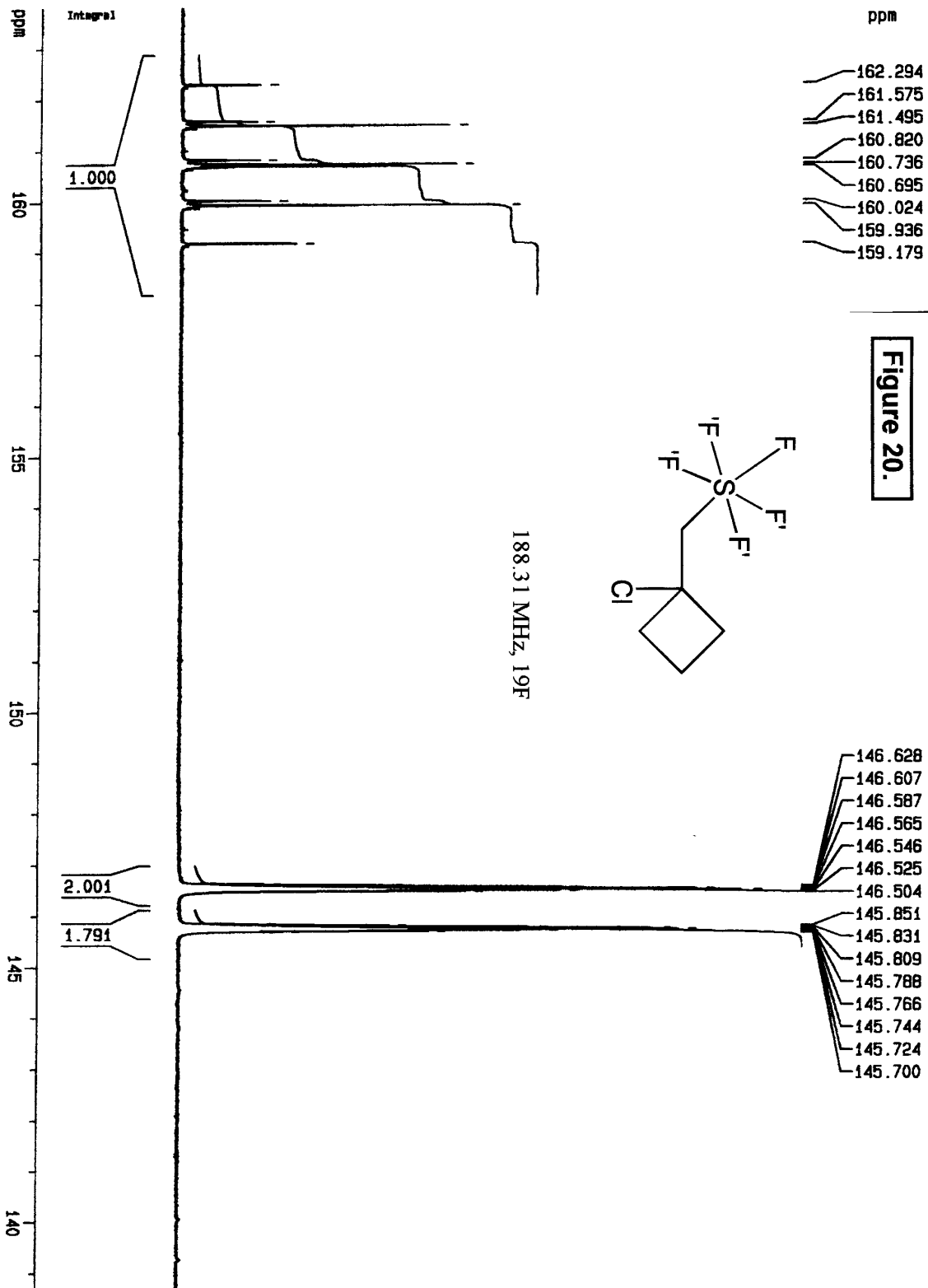
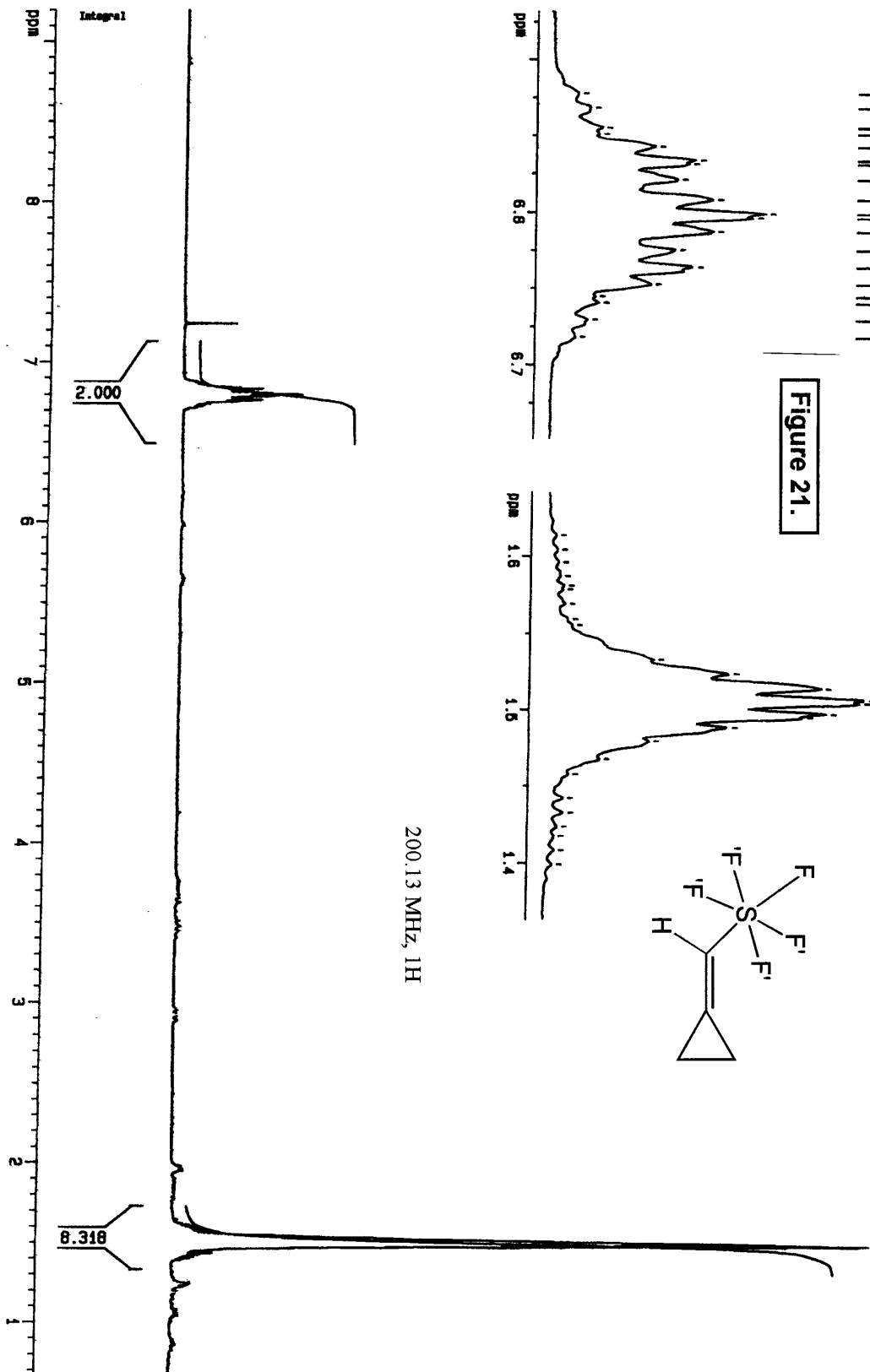




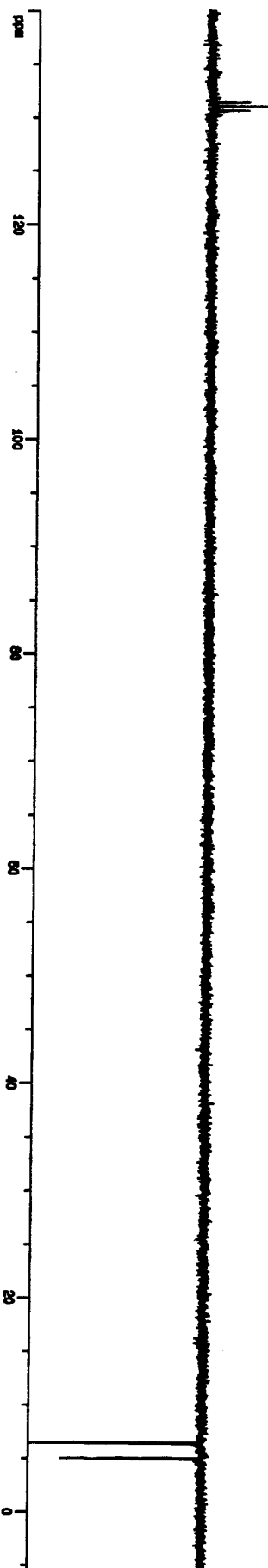
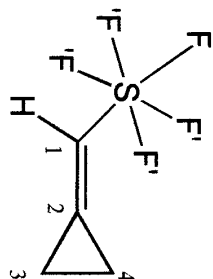
Figure 21.

200.13 MHz, 1H



CH-, CH3- -up, CH2- -down

Figure 22.

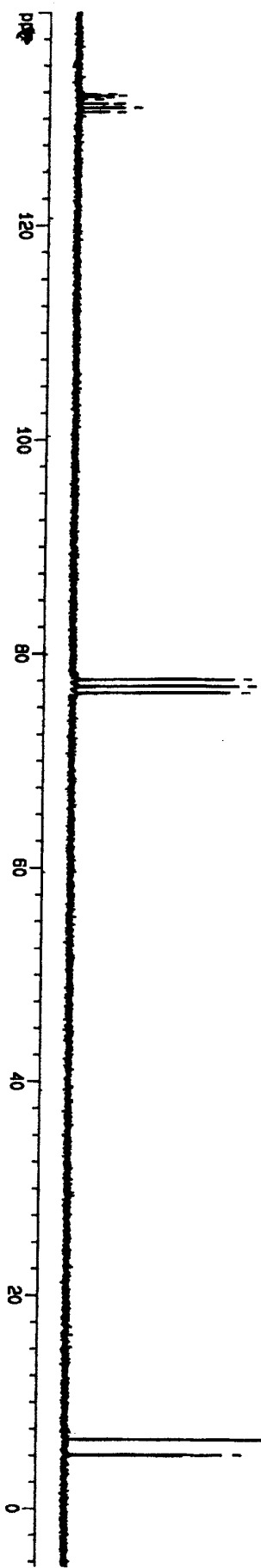


ppm  
132.286  
132.141  
131.997  
131.798  
131.402  
131.369  
131.005  
130.973  
130.609  
130.576

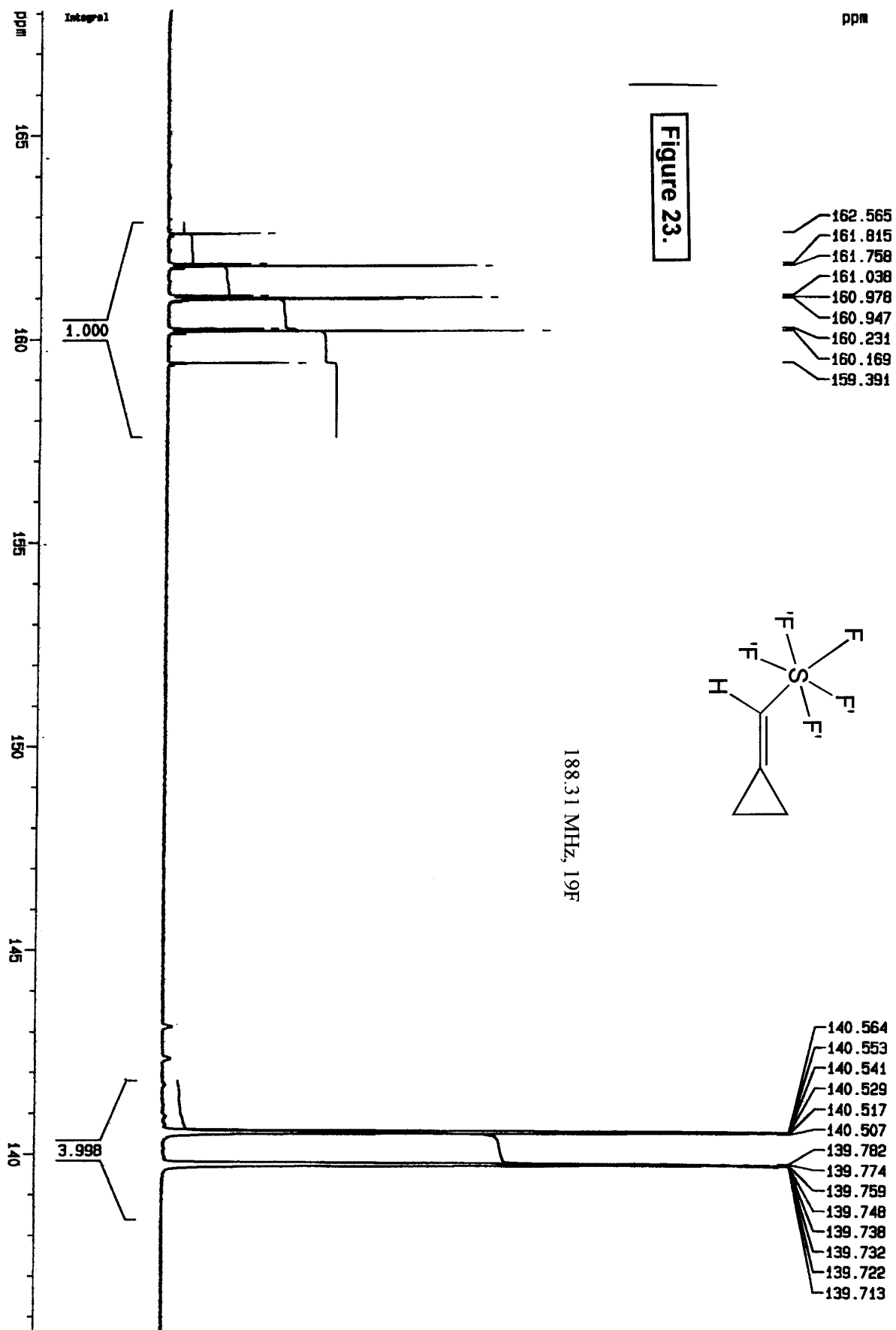
50.3 MHz 13C  
F-22

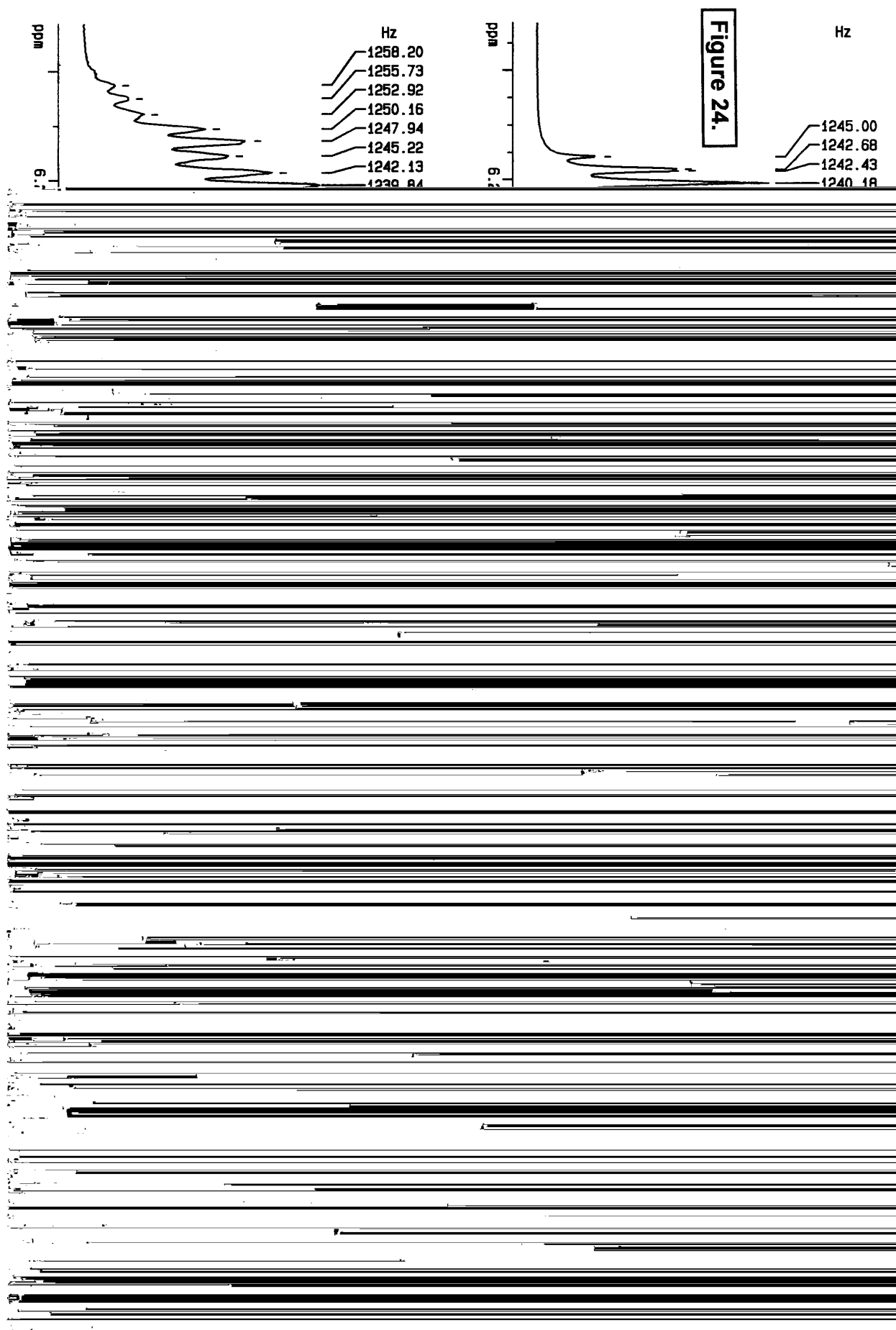
77.577  
76.941  
76.306

6.483  
5.048  
5.033  
5.015



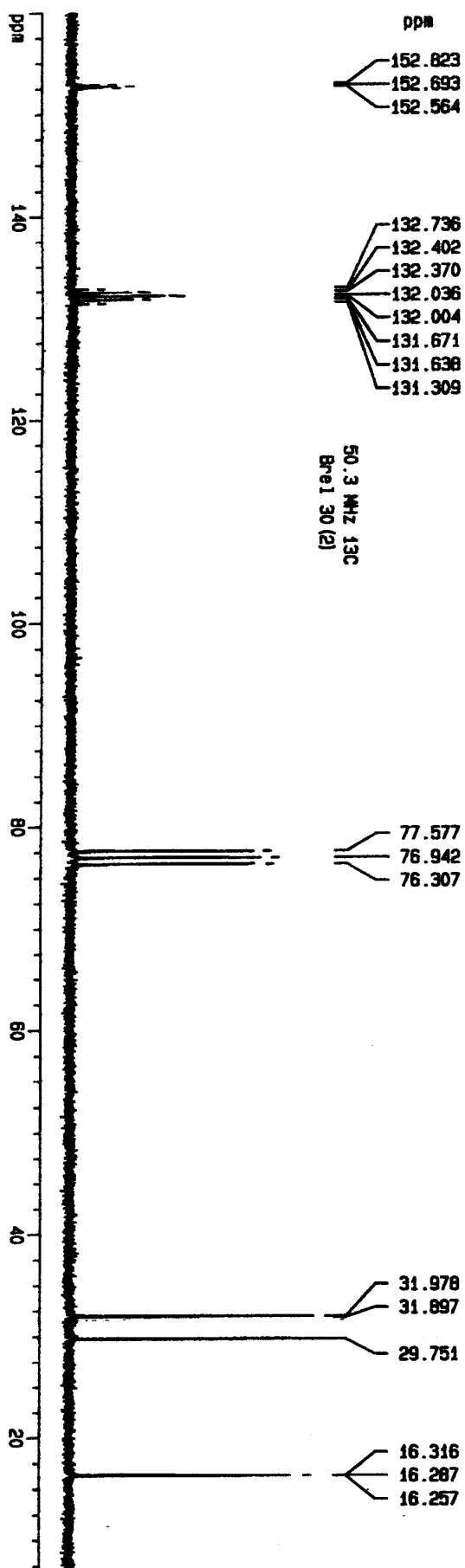
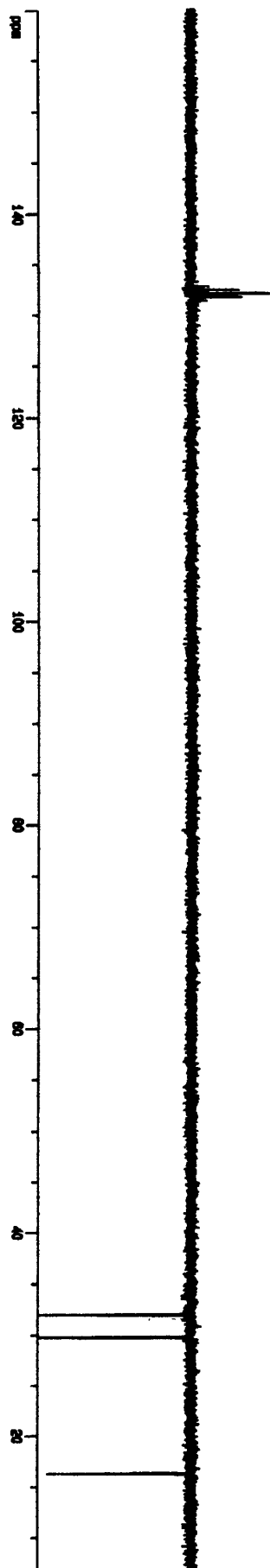
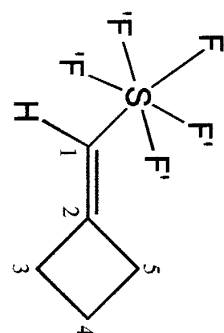






CH-, CH3--up, CH2--down

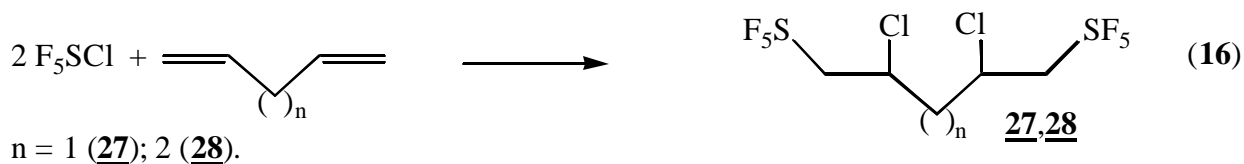
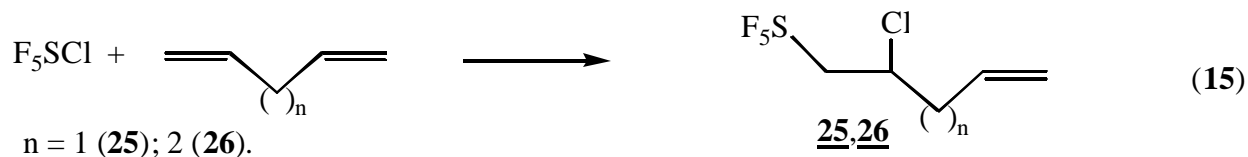
Figure 25.



### 3.1.3. Interaction of SF<sub>5</sub>Cl with 1,4- and 1,5-alkadienes.

Our interest in developing synthetic approach with view in synthesize new derivatives of the interesting unsaturated system with pentafluorothio groups led us to investigate the reaction of pentafluorothio chloride with 1,4- and 1,5-alkadienes.

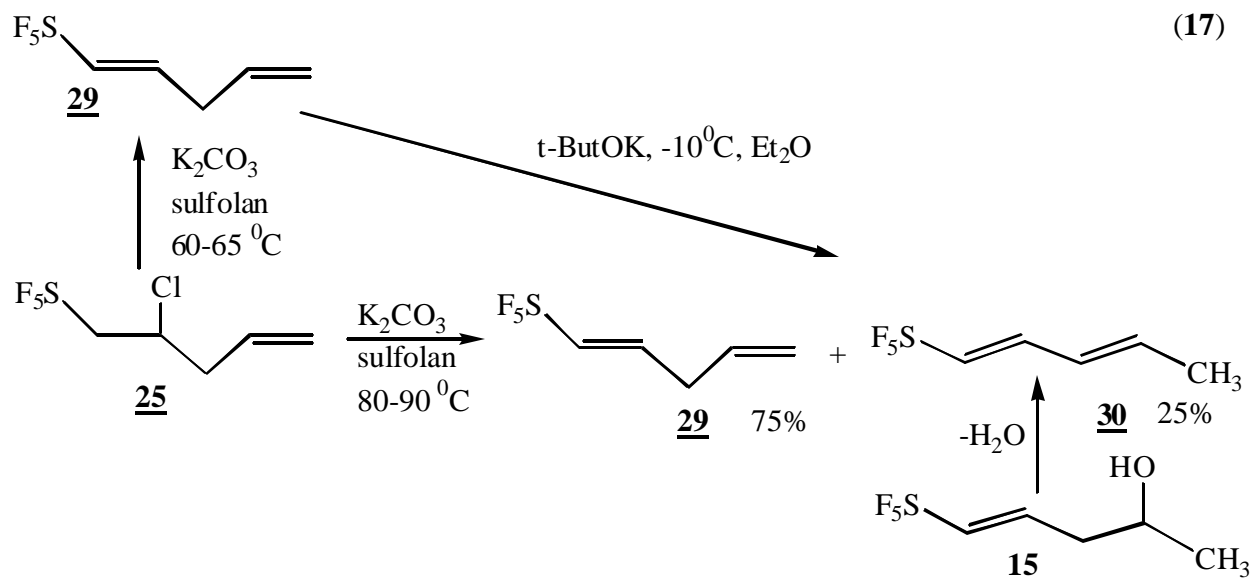
Irradiation (quartz mercury lamp) of 1,4- and 1,5-alkadienes and pentafluorothio chloride in trifluorochloromethane led to adducts **25-28**. The direction of the photochemical addition is regiospecific, F<sub>5</sub>S-radical adds only to terminal methylene groups. Depending on a ratio of 1,5-alkadienes and pentafluorothio chloride we synthesized adducts with one (**25,26**) or two (**27,28**) pentafluorothio group. Reactions were monitored by <sup>19</sup>F NMR spectral data. Compounds **25-28** were isolated as stable, colorless liquid by distillation.



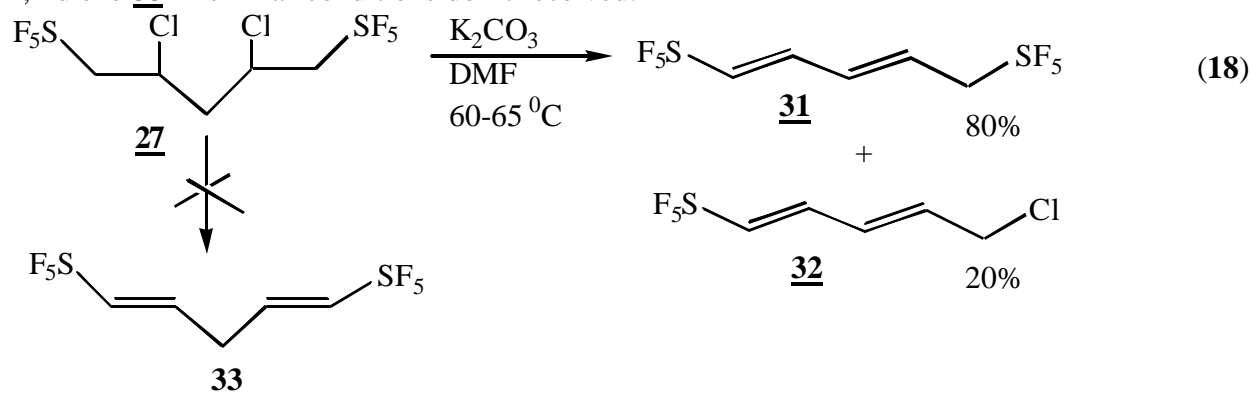
Compounds **25-28** were identified by IR and <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, NMR spectral data. The <sup>1</sup>H NMR spectrums of adducts **25-28** containing signals of the protons at 4.5 ppm (–CClH), signals of the methylene protons at 4.1 ppm (SF<sub>5</sub>CH<sub>2</sub>) and signal other groups containing of protons. The chemical shift and coupling values are in line with those found for other SF<sub>5</sub>CH<sub>2</sub> systems. [18] The <sup>19</sup>F NMR spectrums of adducts **25-28** showed for the SF<sub>5</sub> group a normal AB<sub>4</sub> pattern (δ<sub>F</sub> ~ 160 ppm; δ<sub>F</sub> ~ 140 ppm) from which the J<sub>A-B</sub> coupling was found to be ≈140 Hz.

On the next step our research was study of reaction of dehydrochlorination for compounds **25-28**. Using reaction of elimination of hydrogen chlorine from compounds **25-28** by means of potassium carbonate in the tetramethylene sulfone, we have found that reaction of dehydrochlorination depend on structure of used adduct and from conditions of realization of reaction. So, when compound **25** were heating at 60-65<sup>0</sup>C, 1-(pentafluoro-λ<sup>6</sup>-sulfanyl)-penta-1,4-diene **29** were isolated by distillation with 67% yield. When reaction has carried out at higher temperature (for example 80-90<sup>0</sup>C), were isolated mixture of two products: 1-(pentafluoro-λ<sup>6</sup>-sulfanyl)penta-1,4-diene **29** and 1-(pentafluoro-λ<sup>6</sup>-sulfanyl)penta-1,3-diene **30**, with 3:1 ratio. We have shown, that the 1,3-pentadiene **30** can be synthesized from alcohol **15** by reaction of elimination of water, or by isomerization of 1-(pentafluoro-λ<sup>6</sup>-sulfanyl)-penta-1,4-diene **29**.

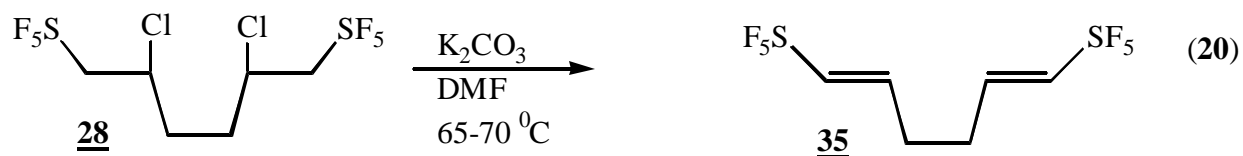
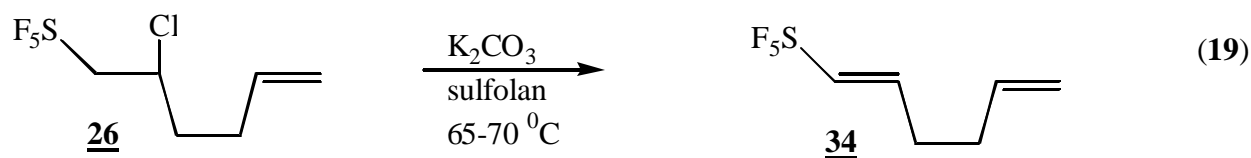
The structure of **29,30** were established and confirmed on the basis of their IR and <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, NMR spectral data.



The unusual result was received at reaction of dehydrochlorination adduct **27**. Using reaction of elimination of hydrogen chlorine from compounds **27** by means of potassium carbonate in the dimethylformamide we synthesized new 1,3-pentadienes with one **32** or two **31** pentafluorosulfanyl ( $\text{SF}_5$ ) group. Formation of expected 1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)penta-1,4-diene **33** in similar conditions don't received.



In the case of adducts **26, 28**, reaction of dehydrochlorination, by means of potassium carbonate in the dimethylformamide or sulfolane following easily and extremely with formation mono- or di-derivative of 1,5-hexadiene.



The structure of **29,30** were established and confirmed on the basis of their IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , NMR spectral data. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of some compounds are shown on Figure 26-48.

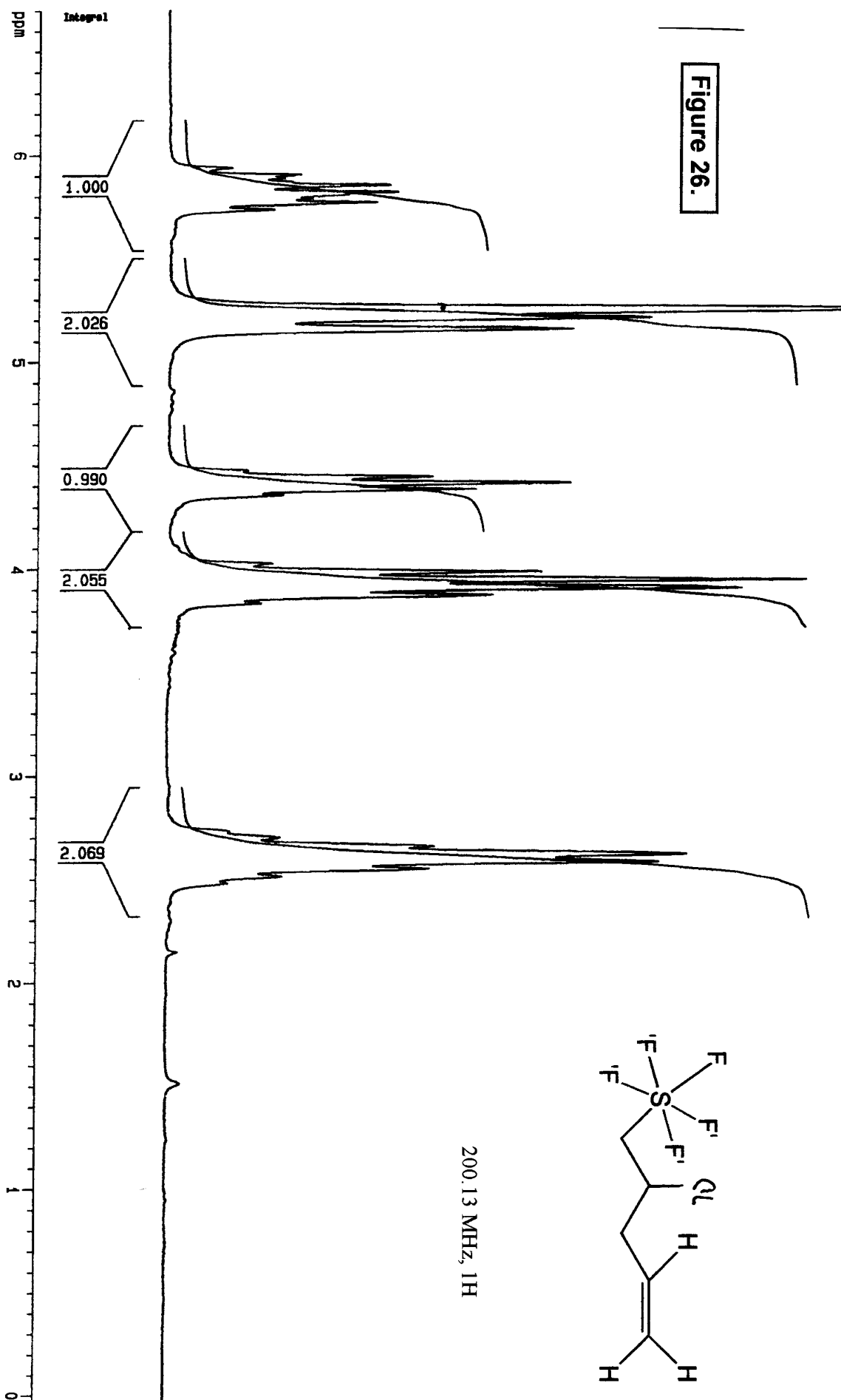
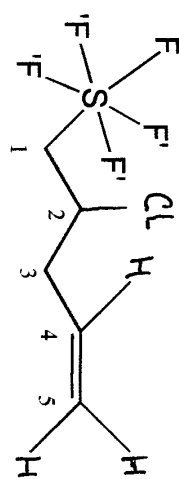
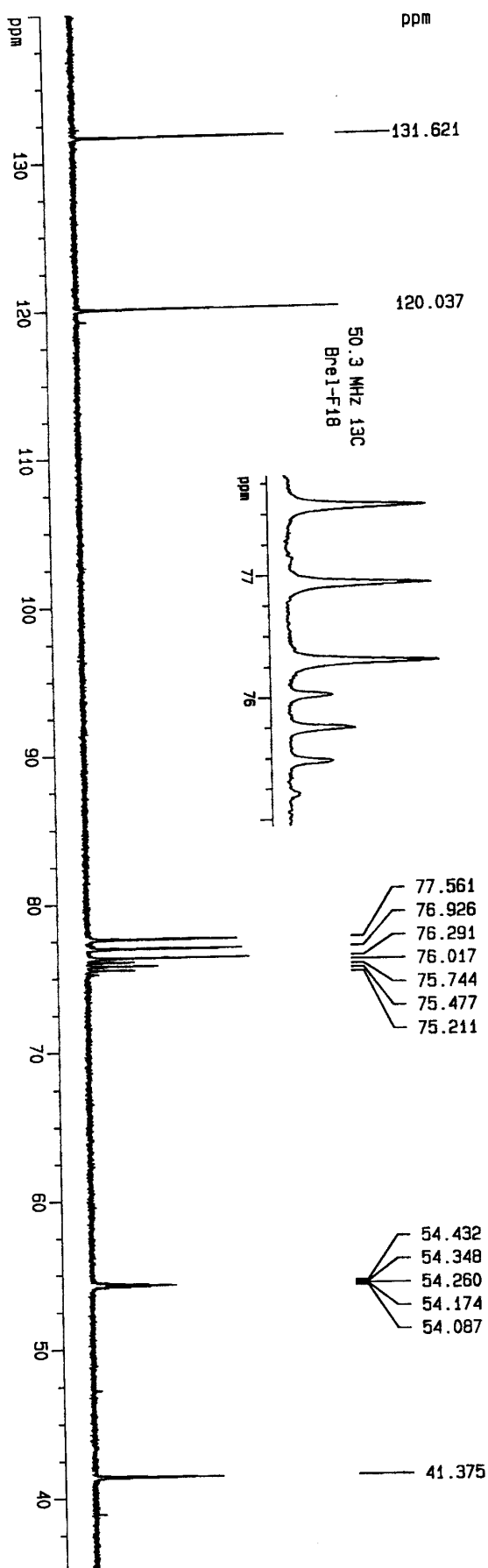
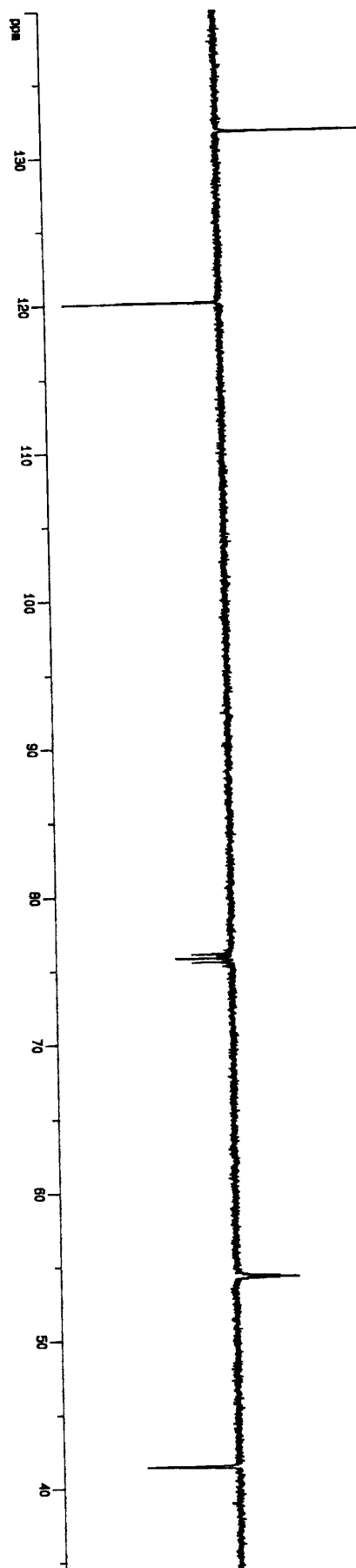


Figure 27.



CH-, CH3- -up, CH2- -down



188.31 MHz  $^{19}\text{F}$   
F-18 (CDCl<sub>3</sub>), ref. CF<sub>3</sub>COOH

Figure 28.

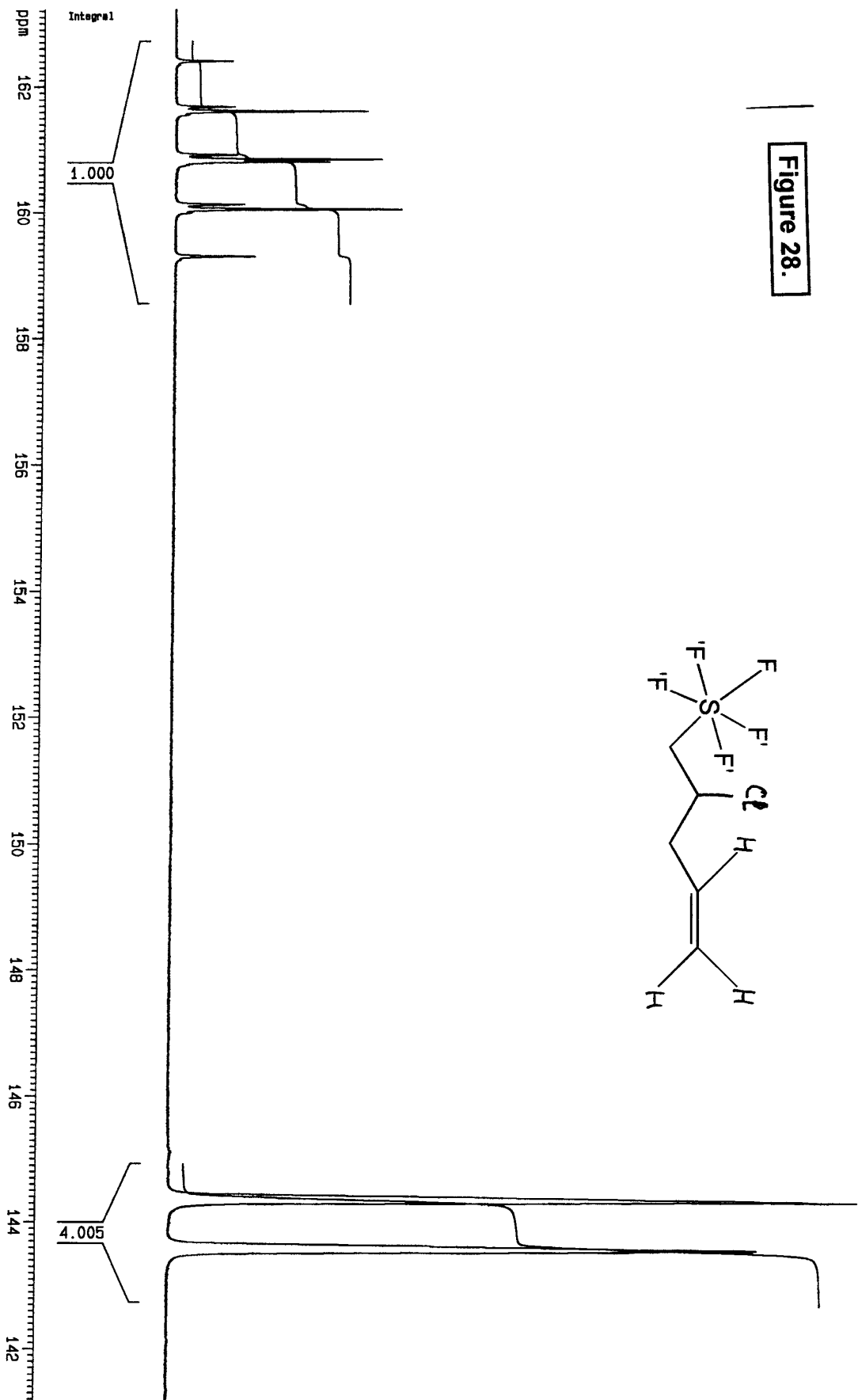
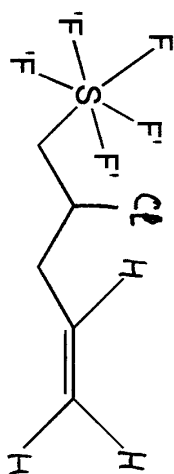
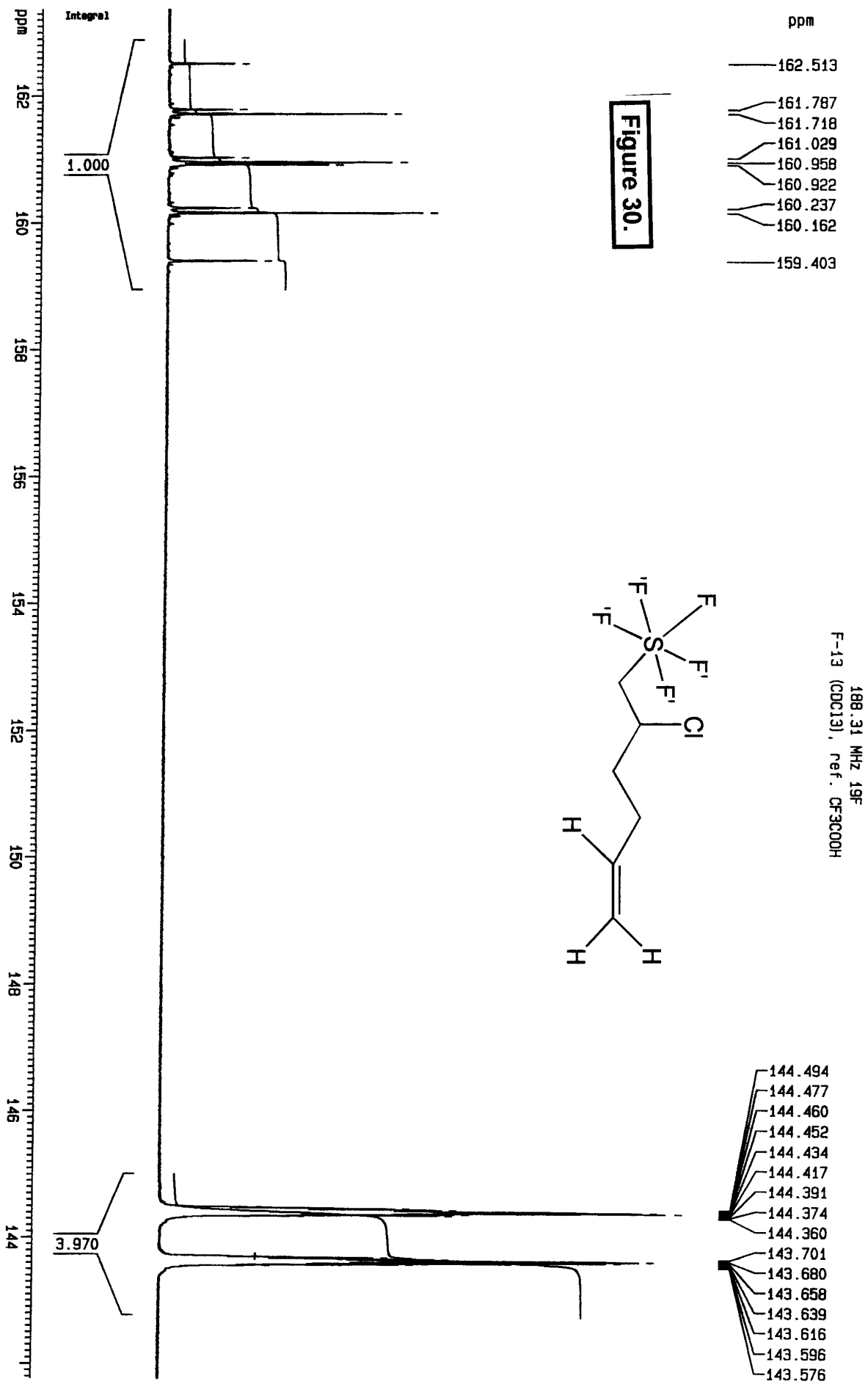
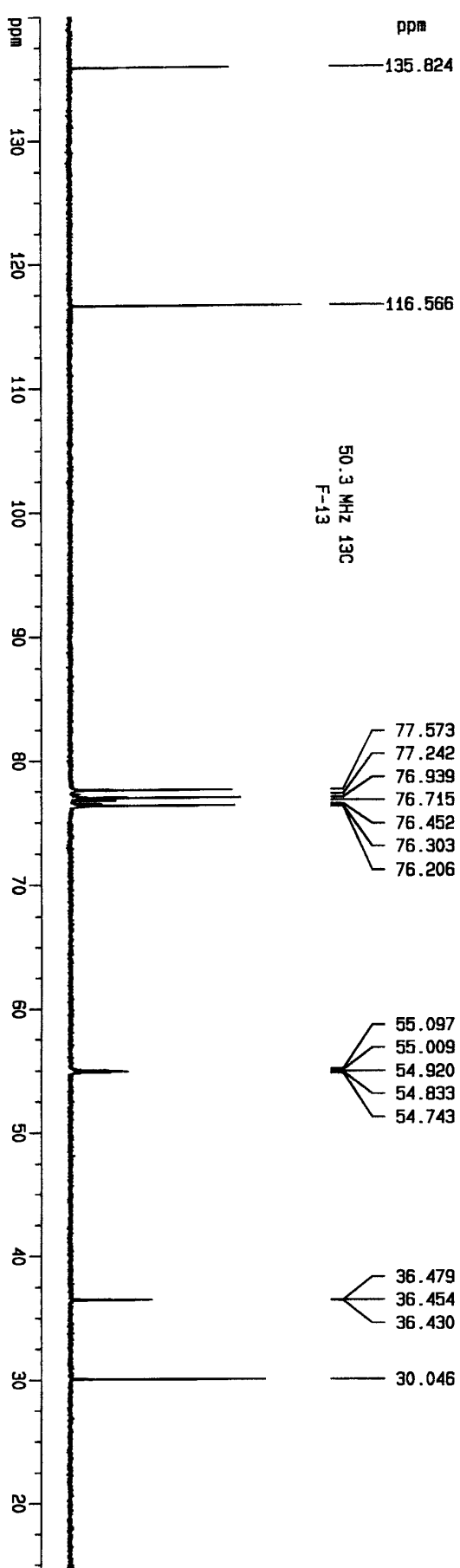
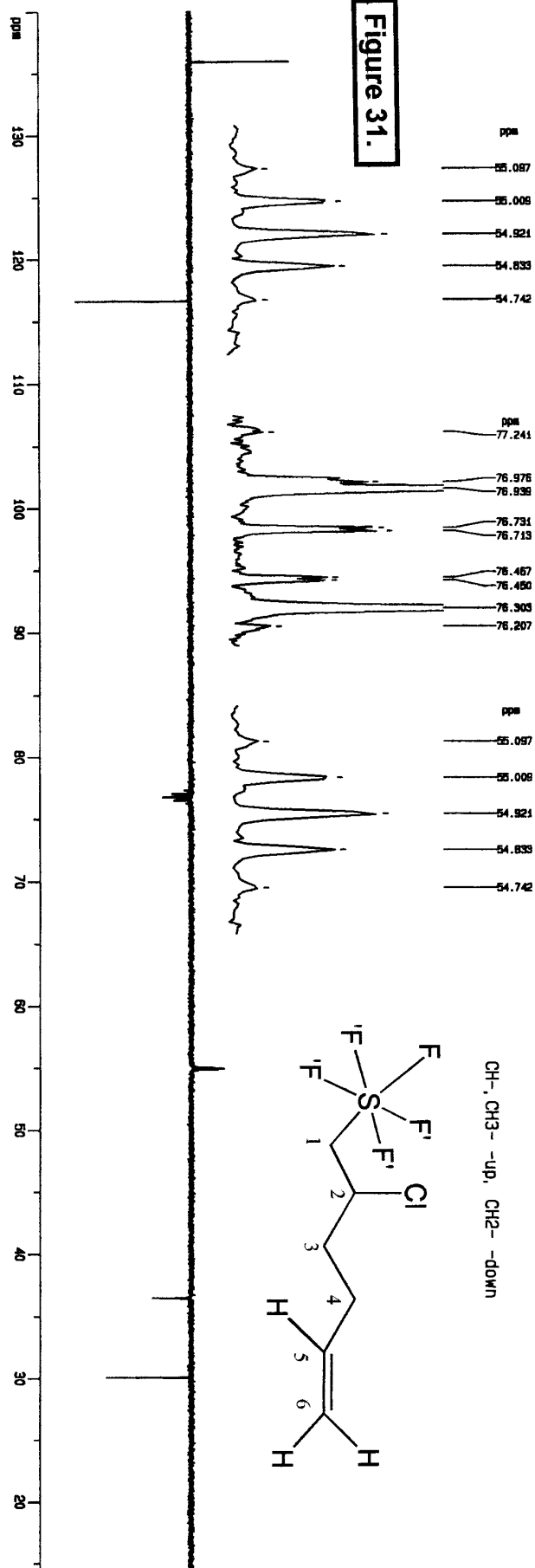






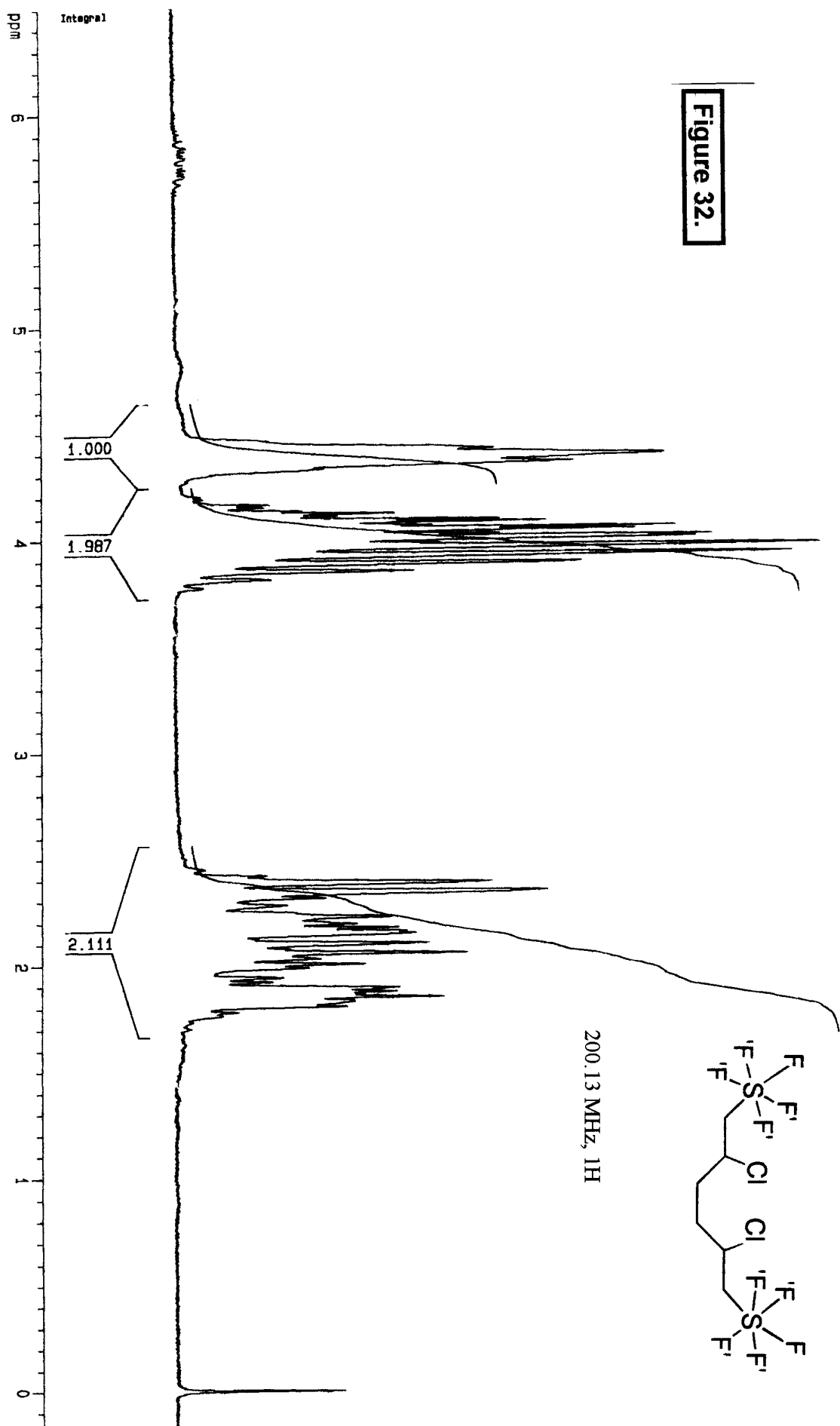
Figure 29.





200.13MHz F-12

Figure 32.



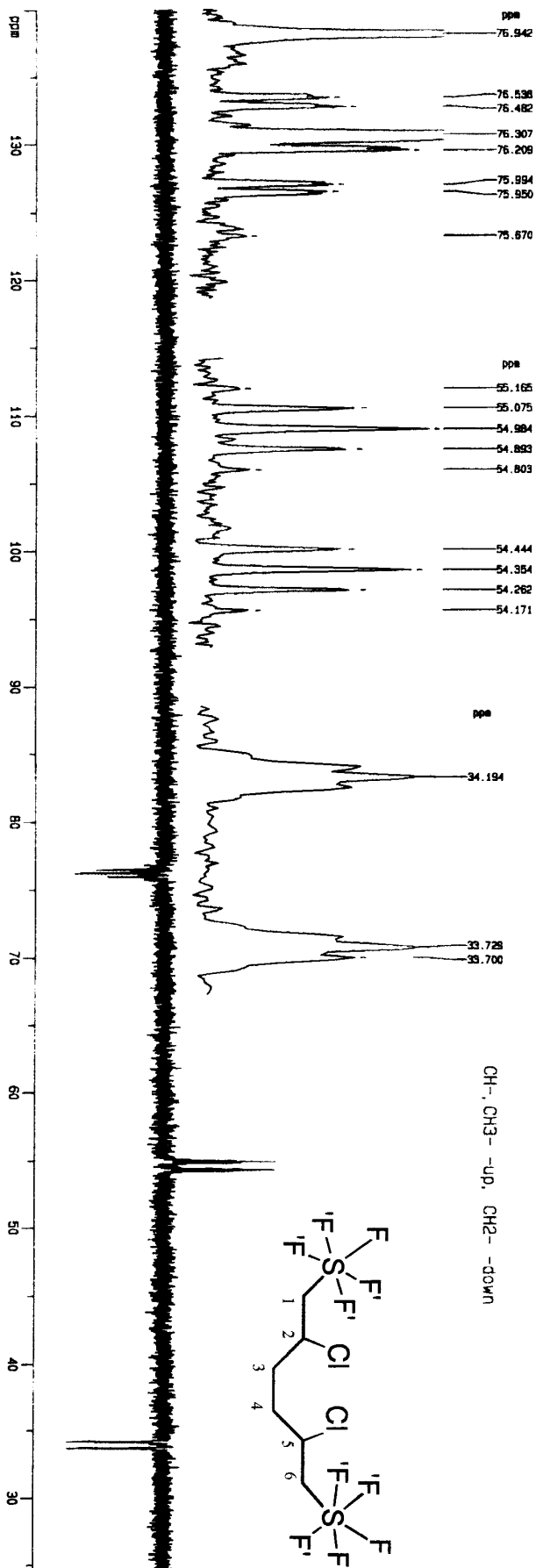
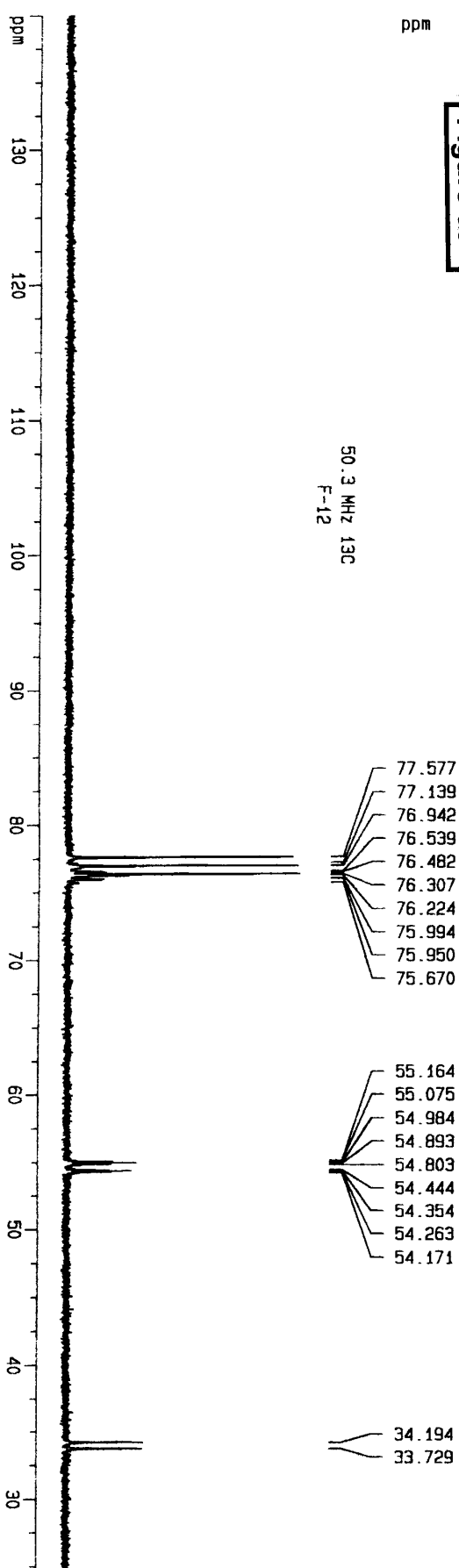


Figure 33.



188.31 MHz  $^{19}\text{F}$   
 $\text{F}-12$  ( $\text{CDCl}_3$ )

**Figure 34.**

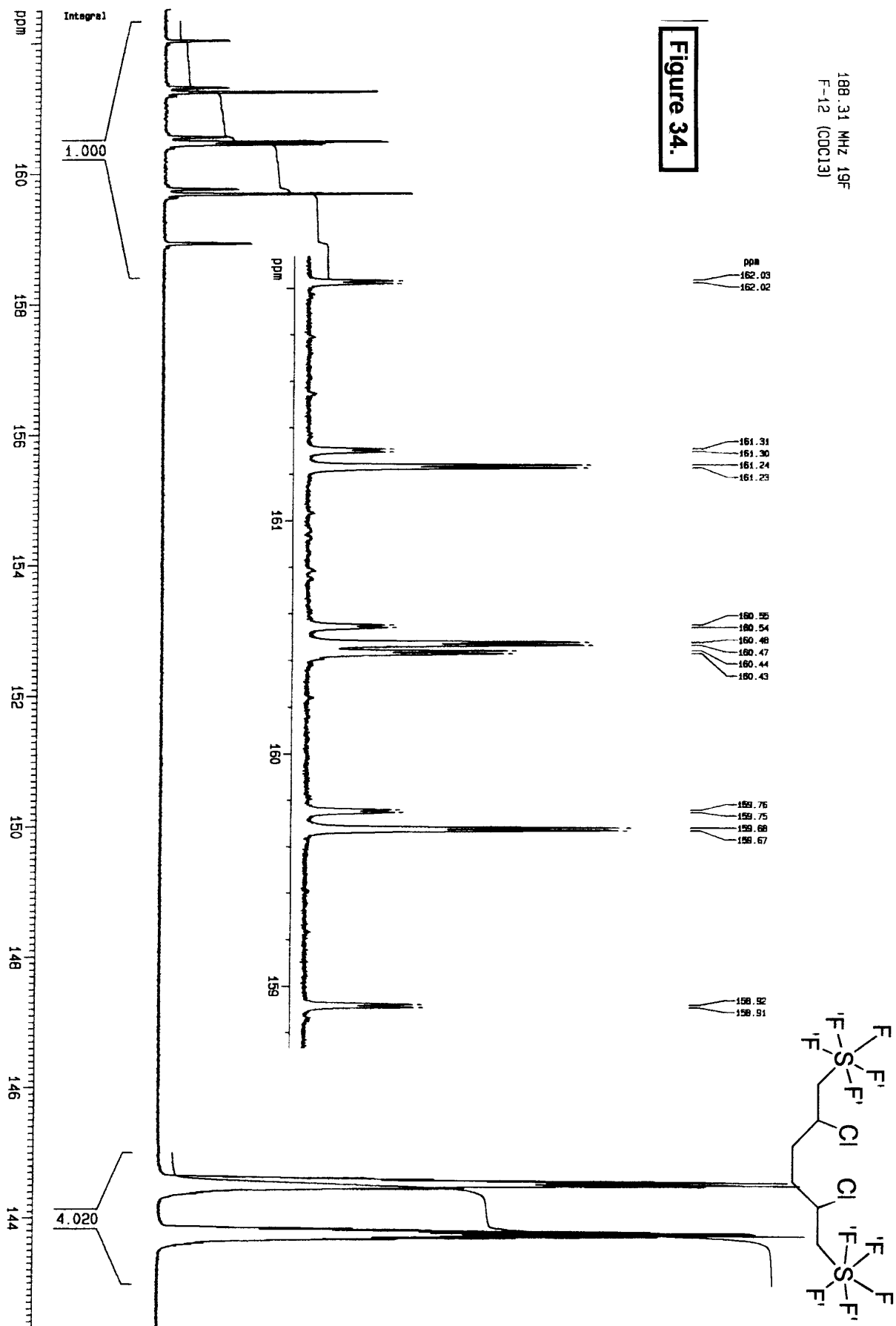
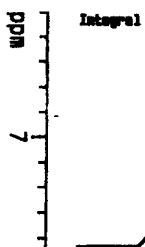
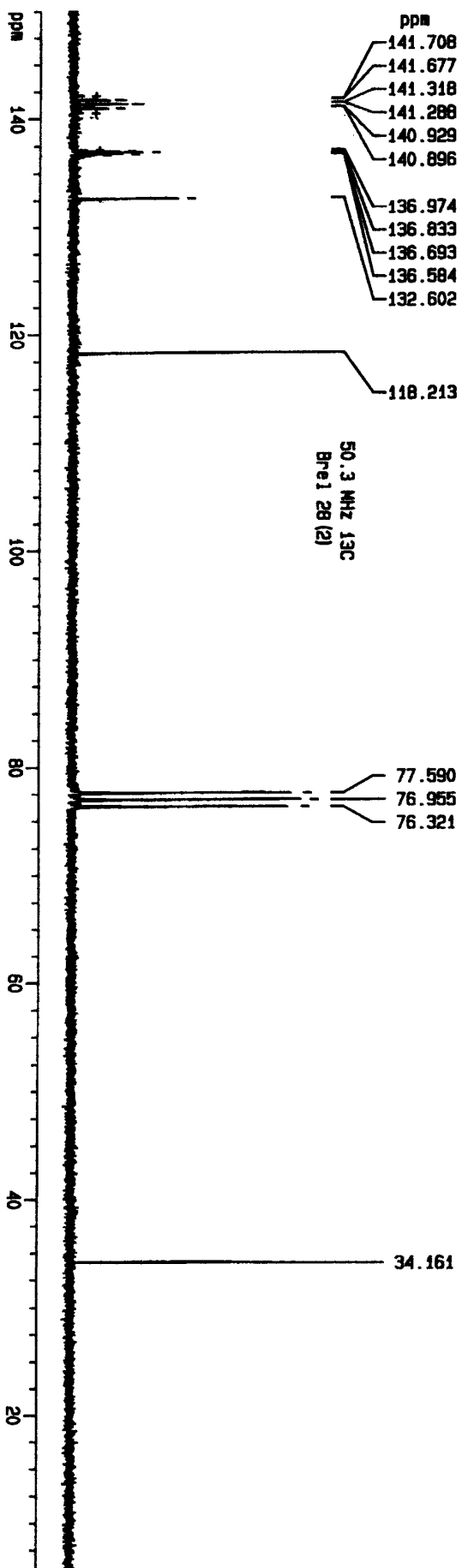
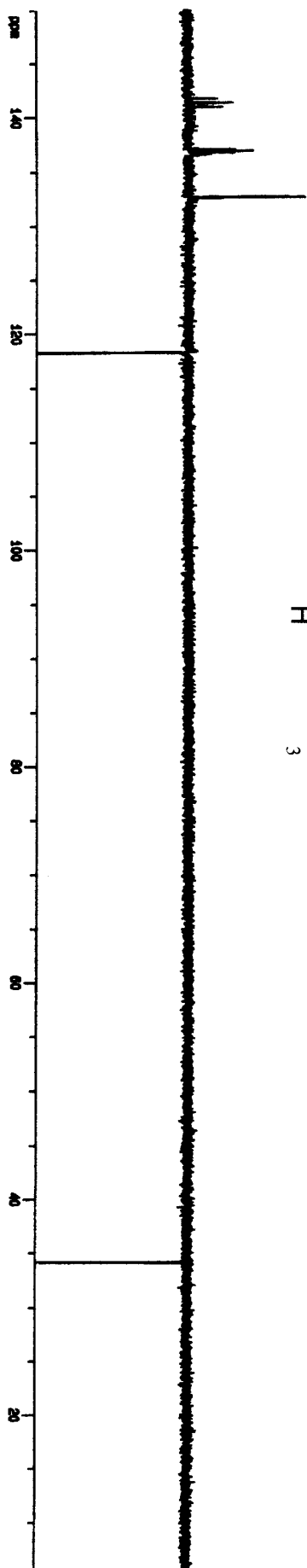
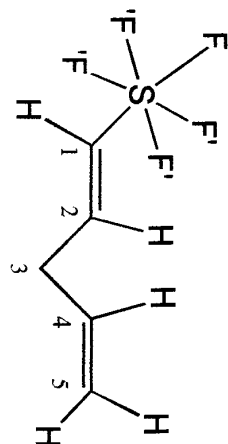


Figure 35.

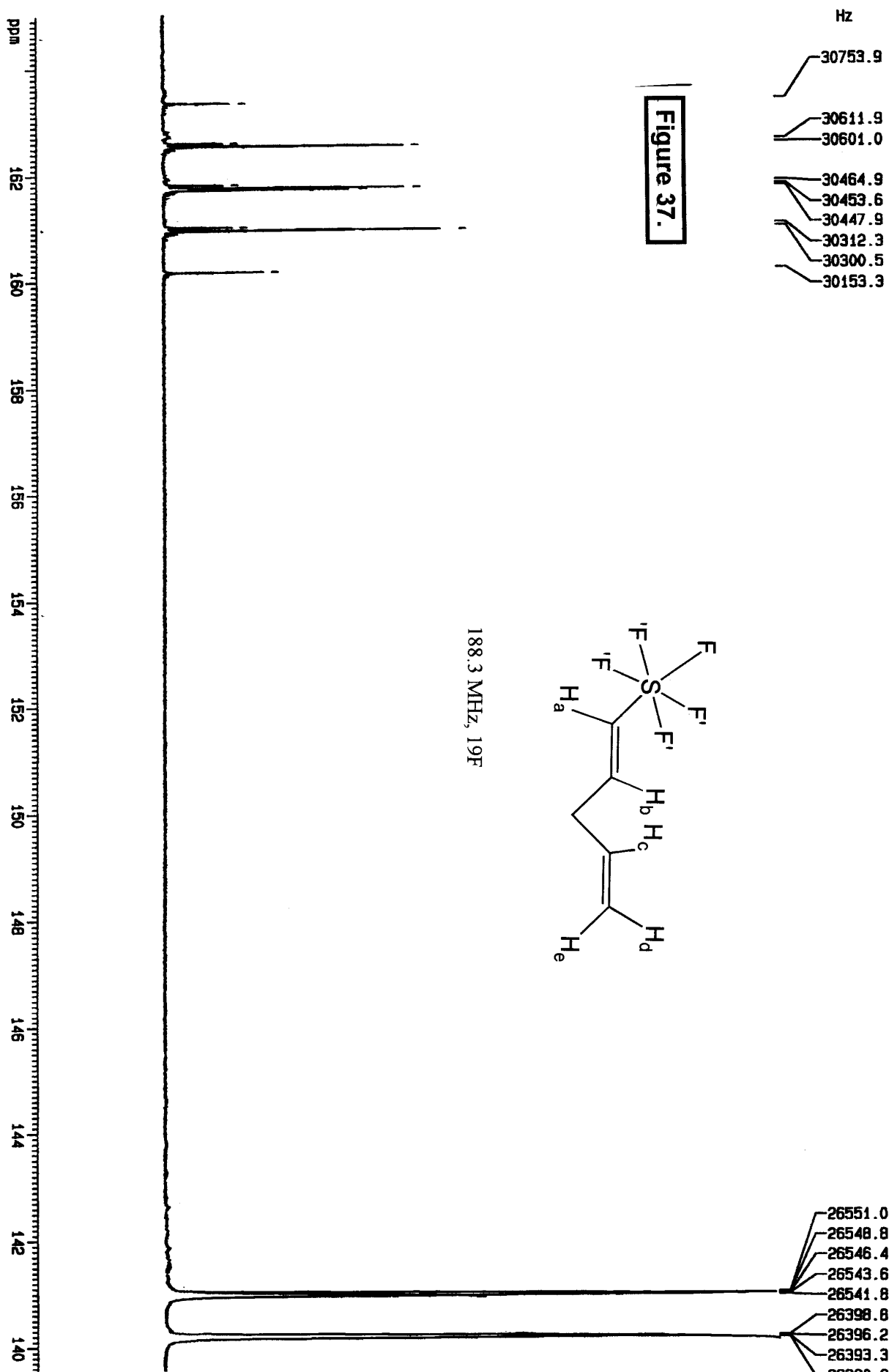


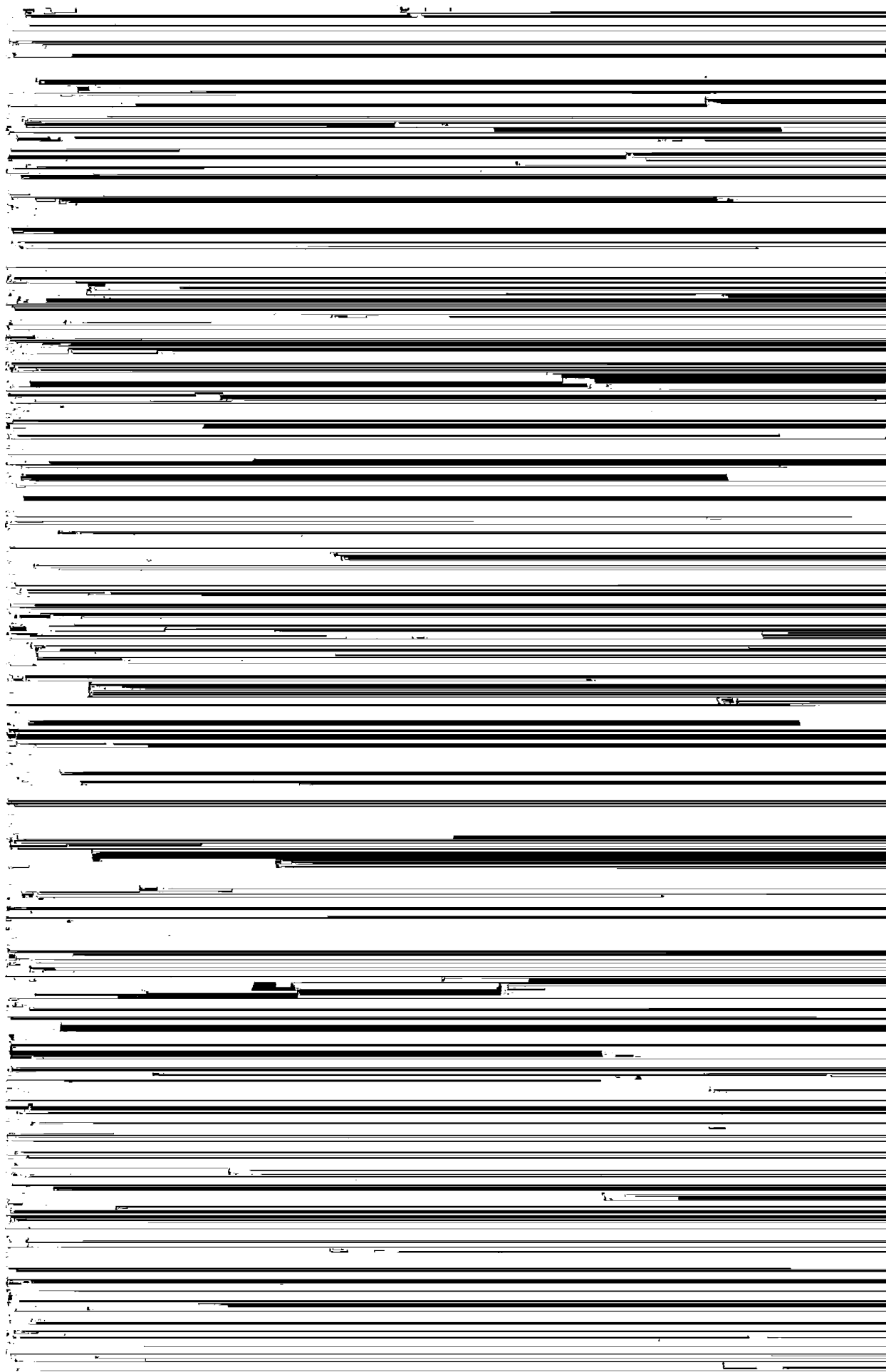
CH-, CH3- -up, CH2- -down

Figure 36.









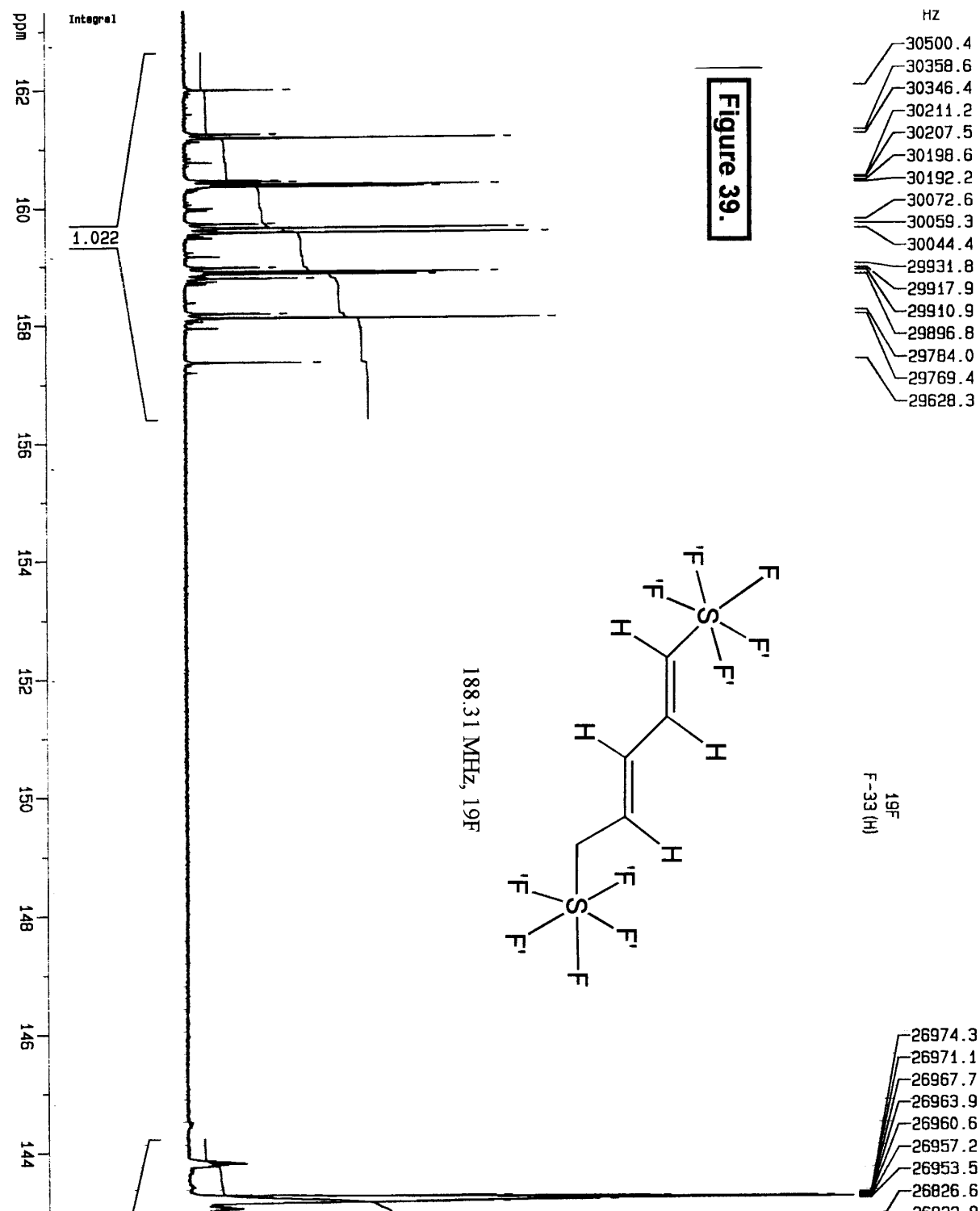
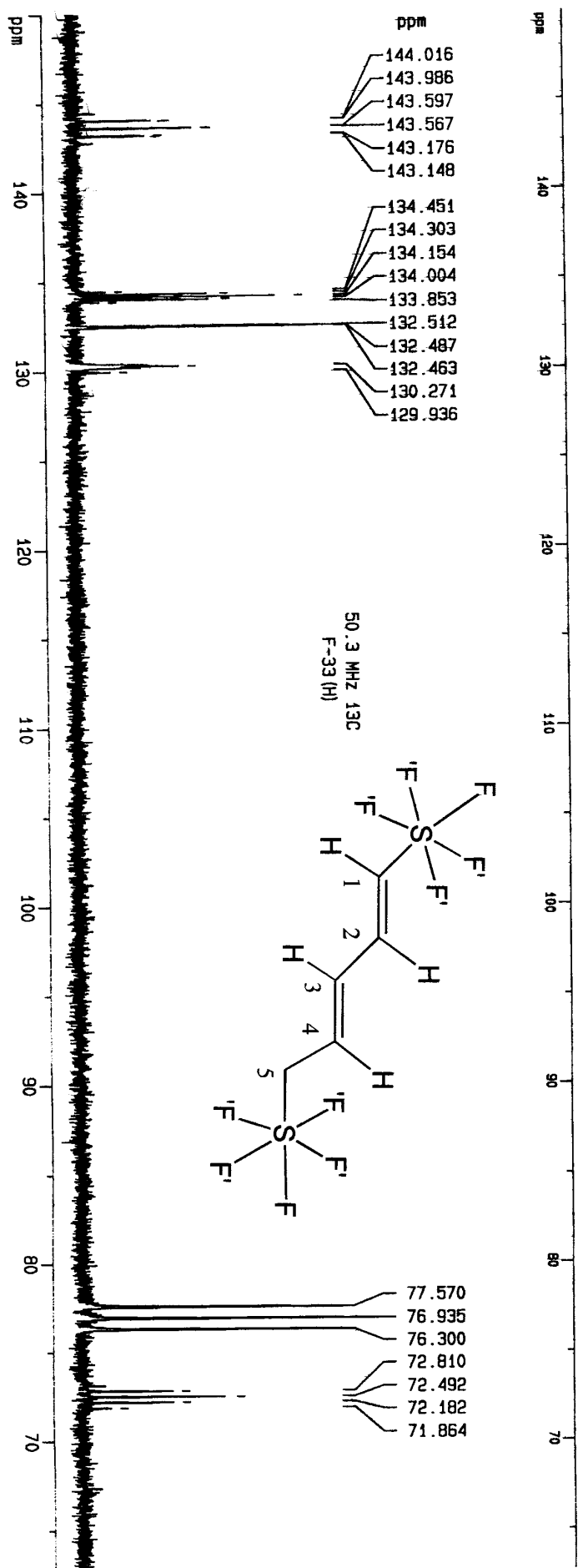
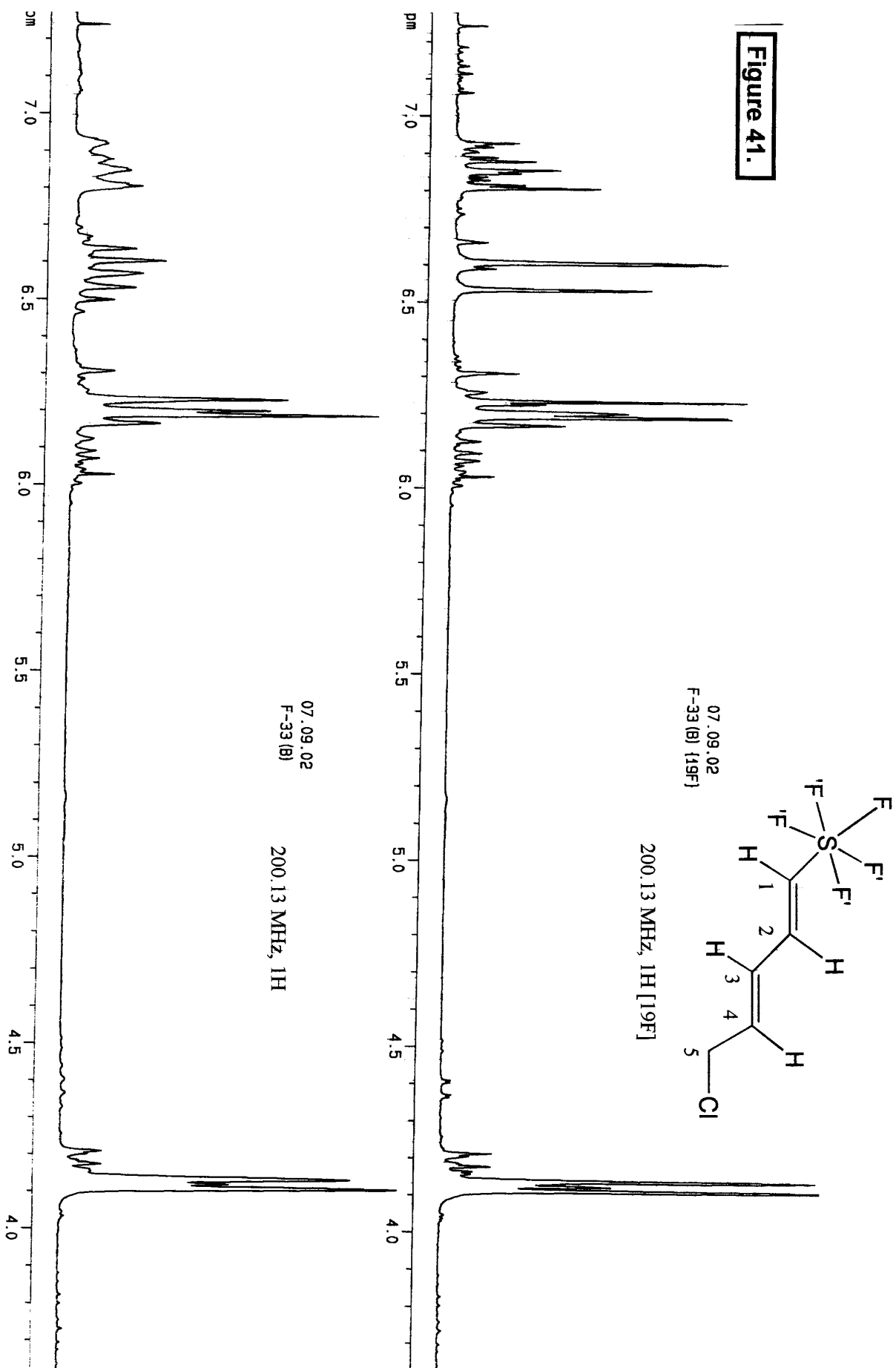


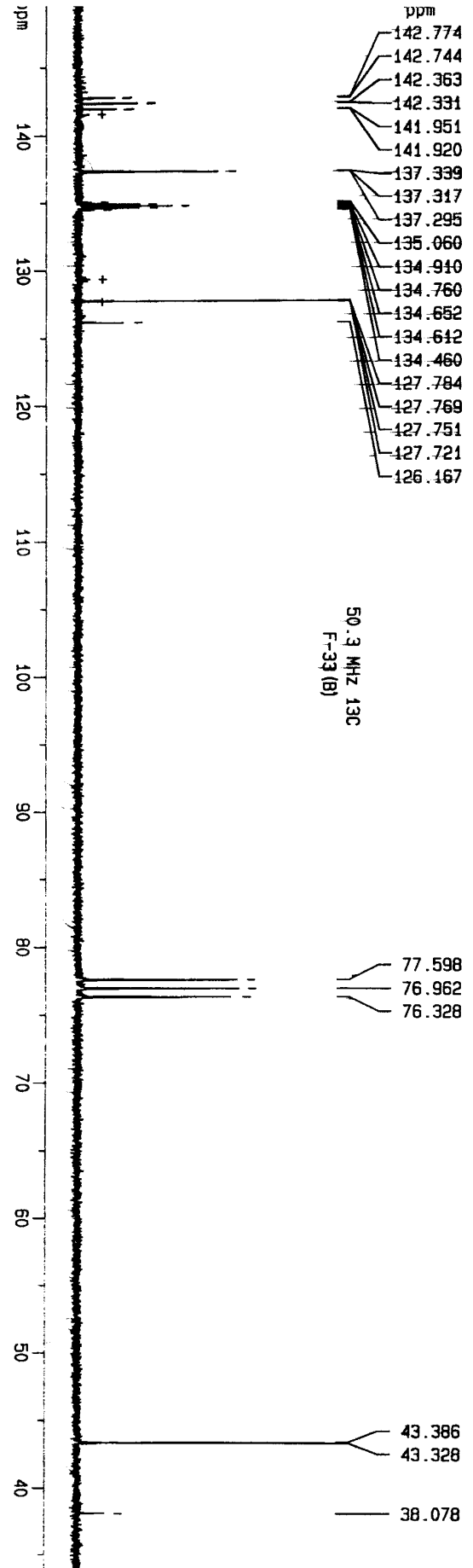
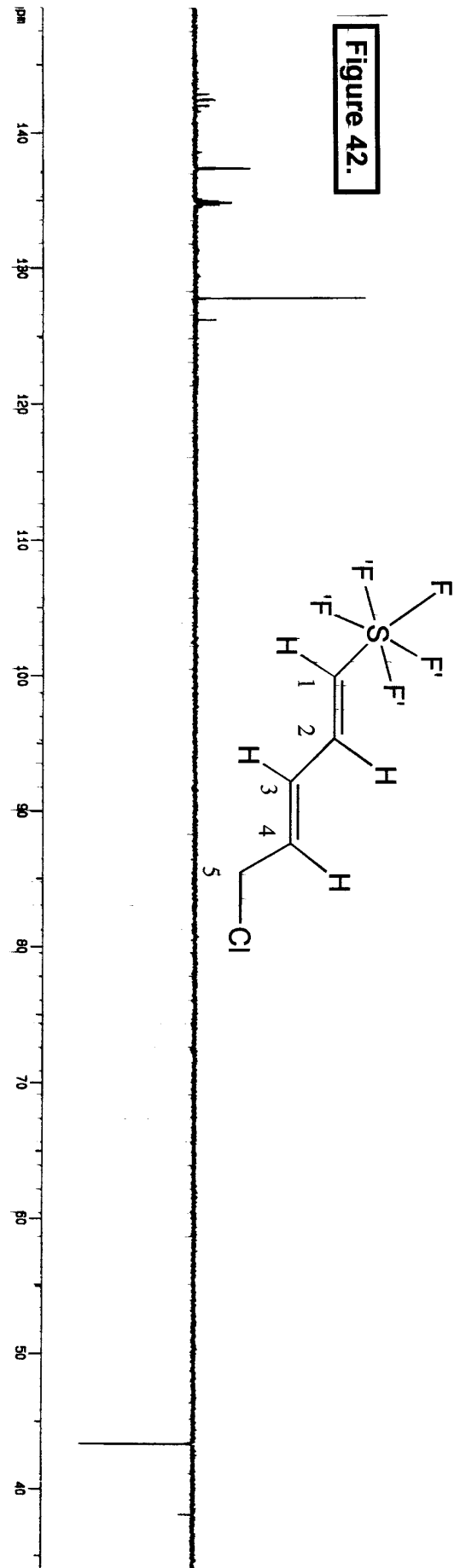
Figure 40.

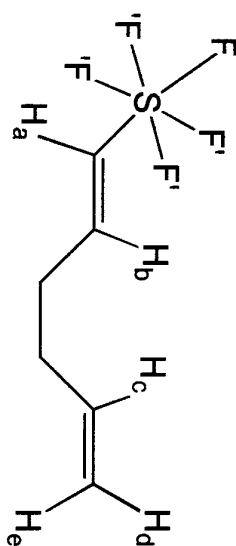


**Figure 41.**

CH-, CH3- -up, CH2- -down

Figure 42.





200.13 MHz, <sup>1</sup>H

Figure 43.

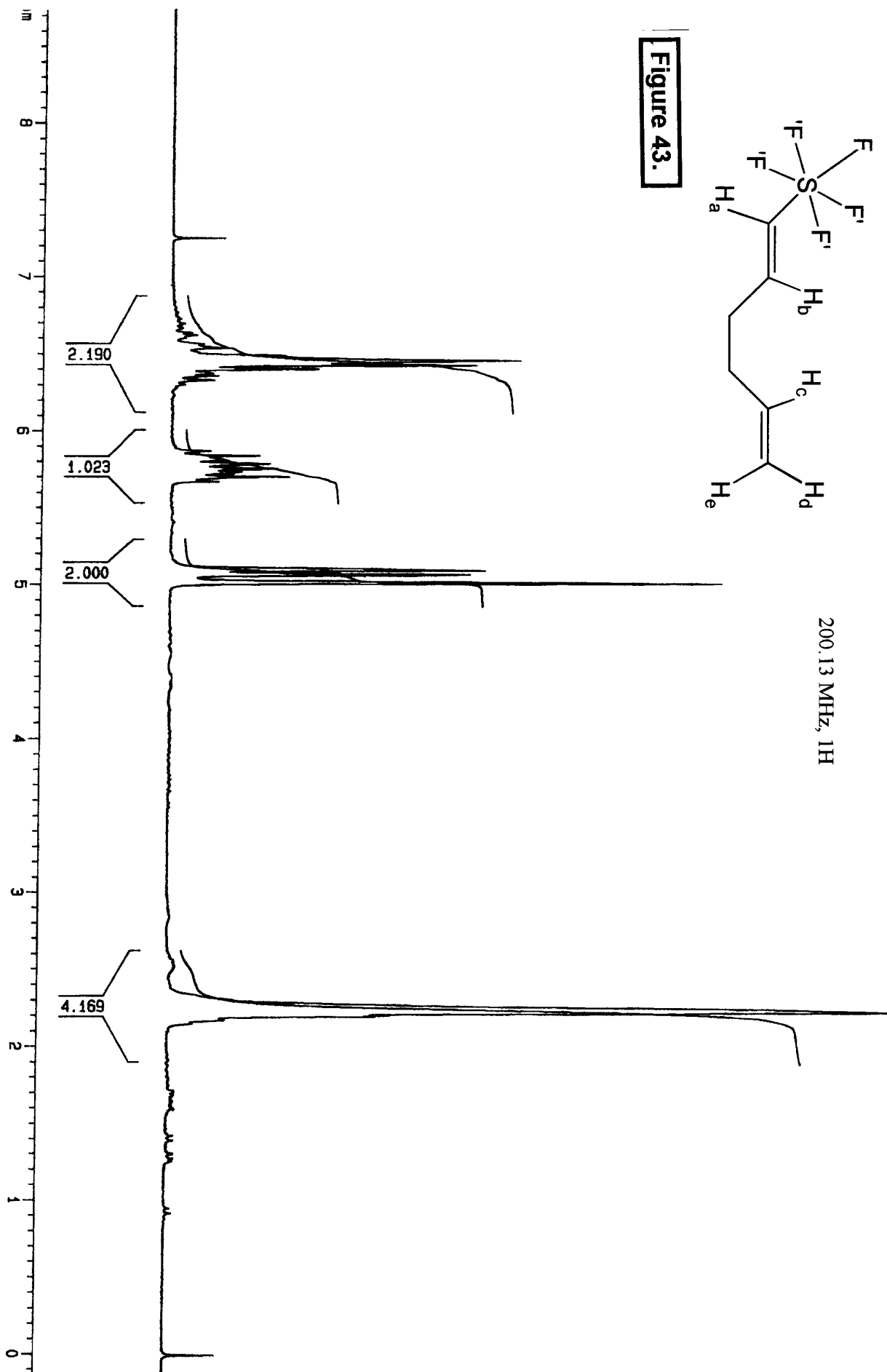
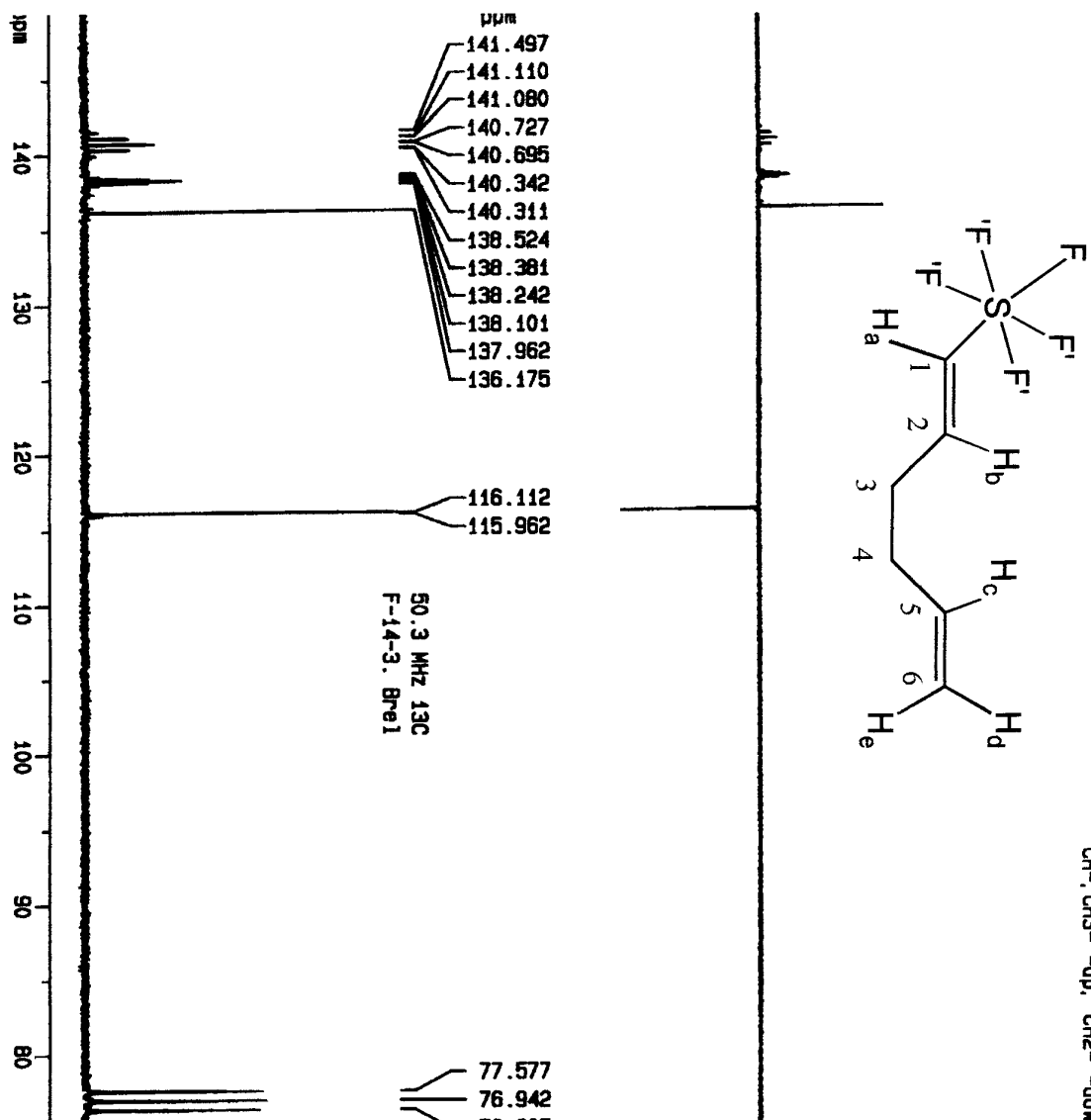


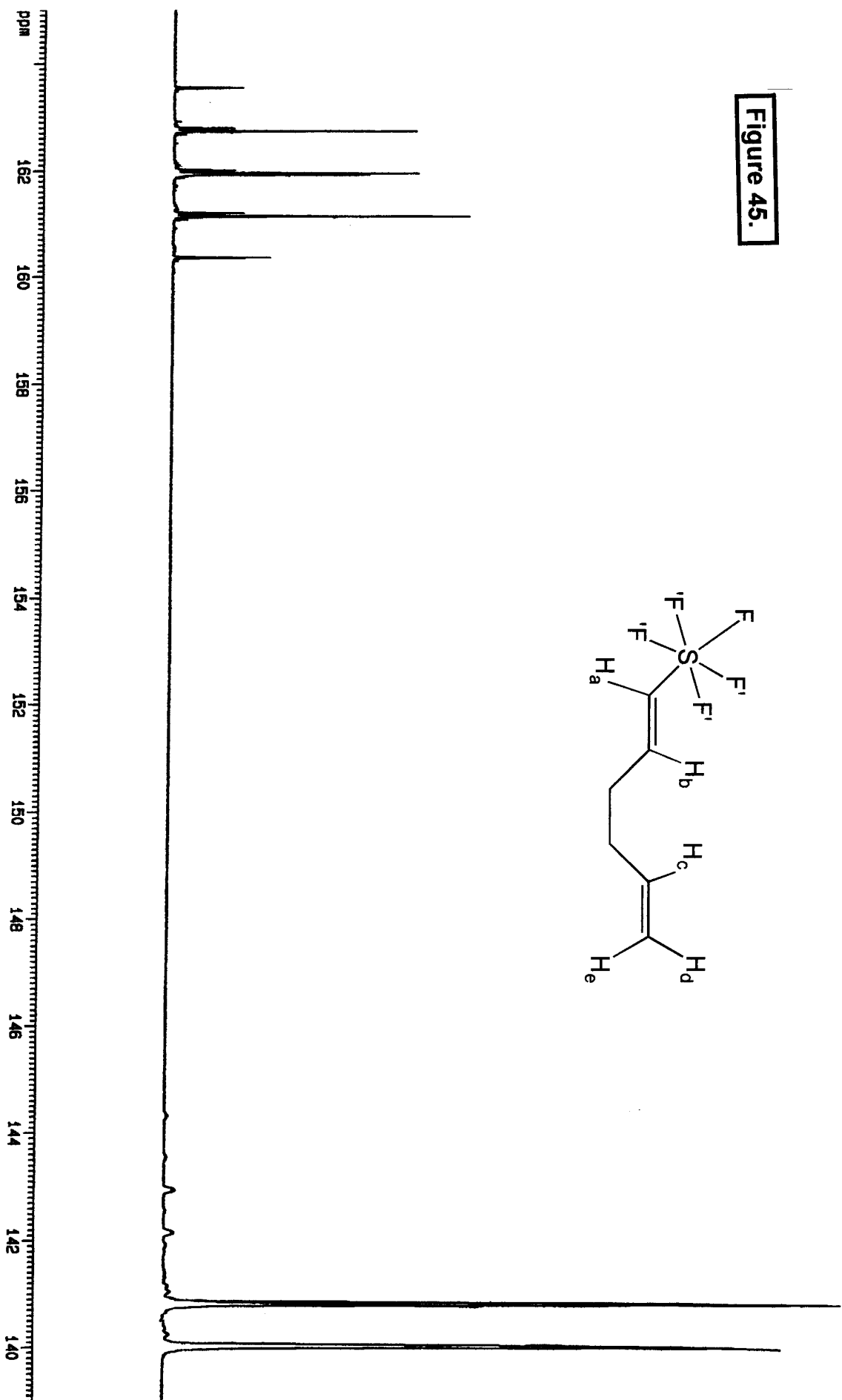
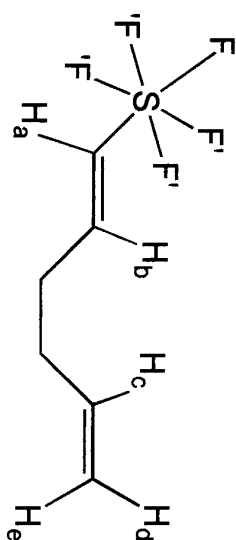
Figure 44.

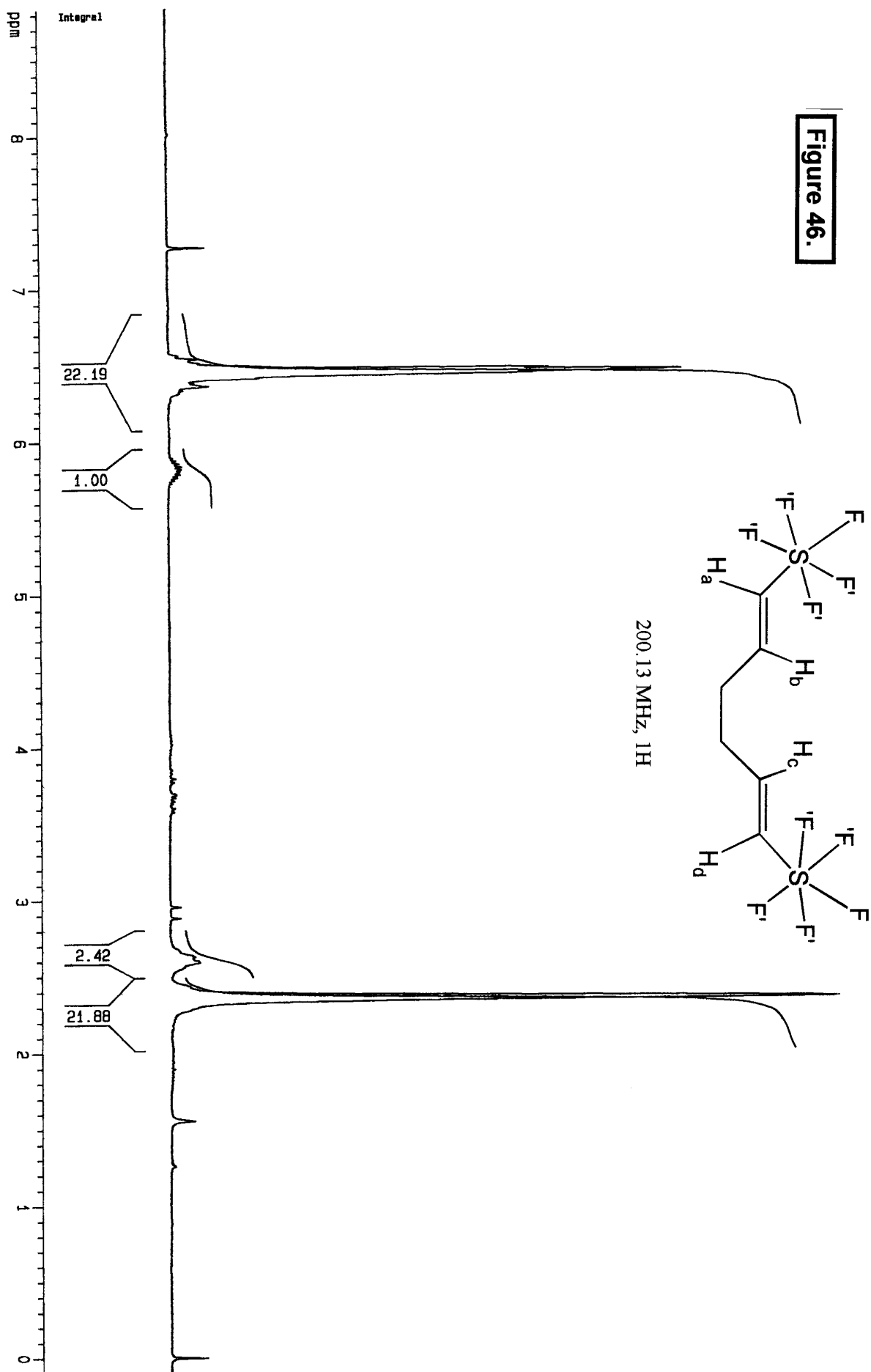




188.31 MHz  $^{19}\text{F}$   
F-14-3 (CDCl<sub>3</sub>), ref. CF<sub>3</sub>COOH

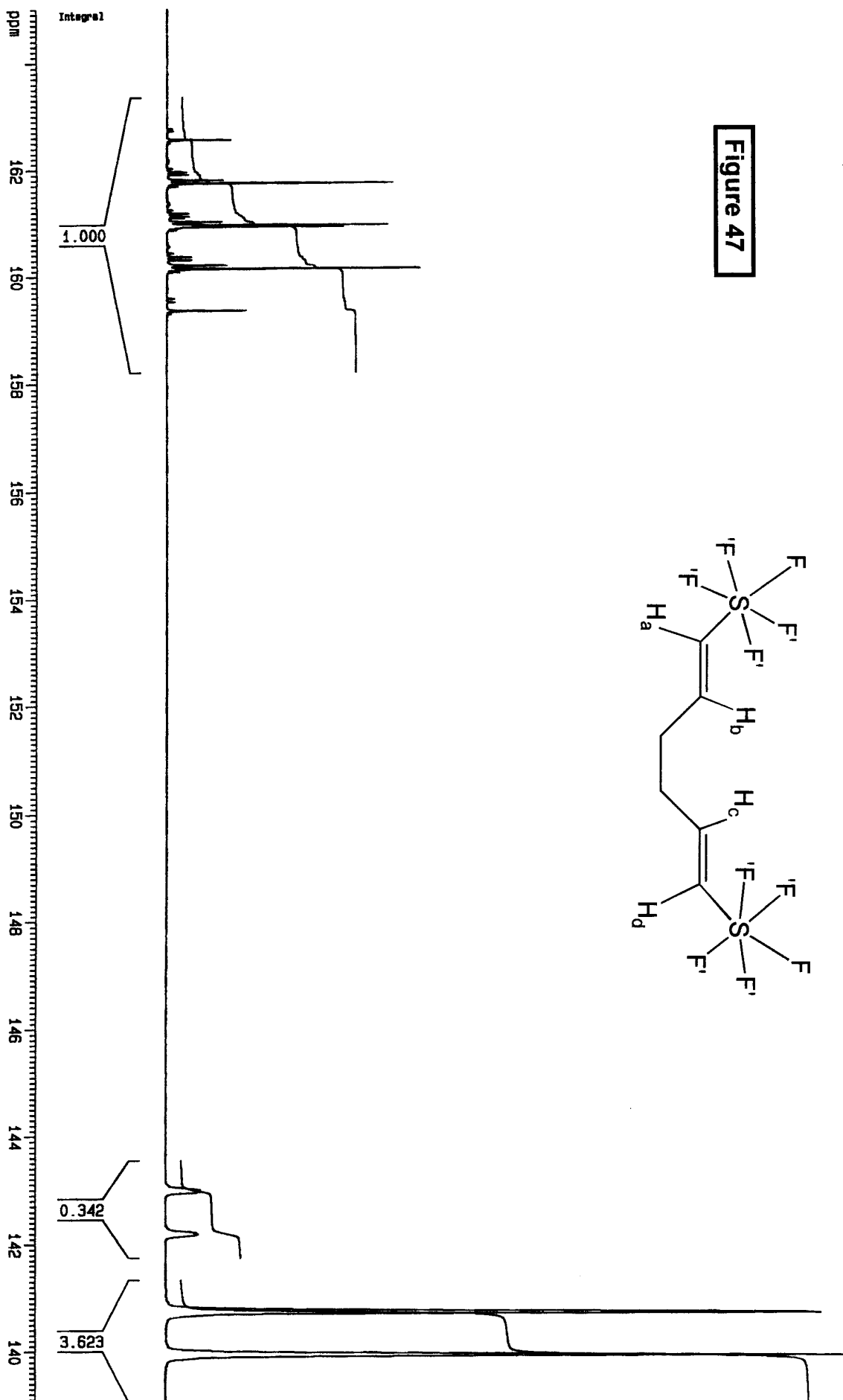
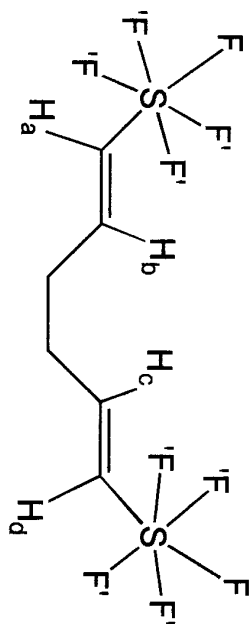
Figure 45.

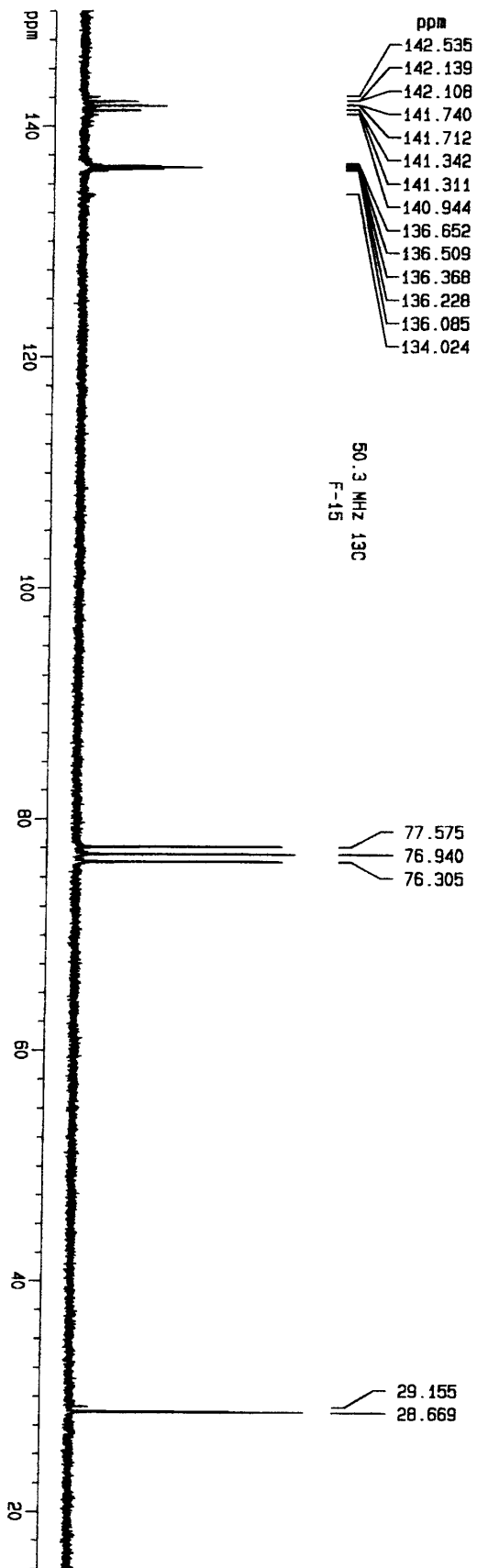
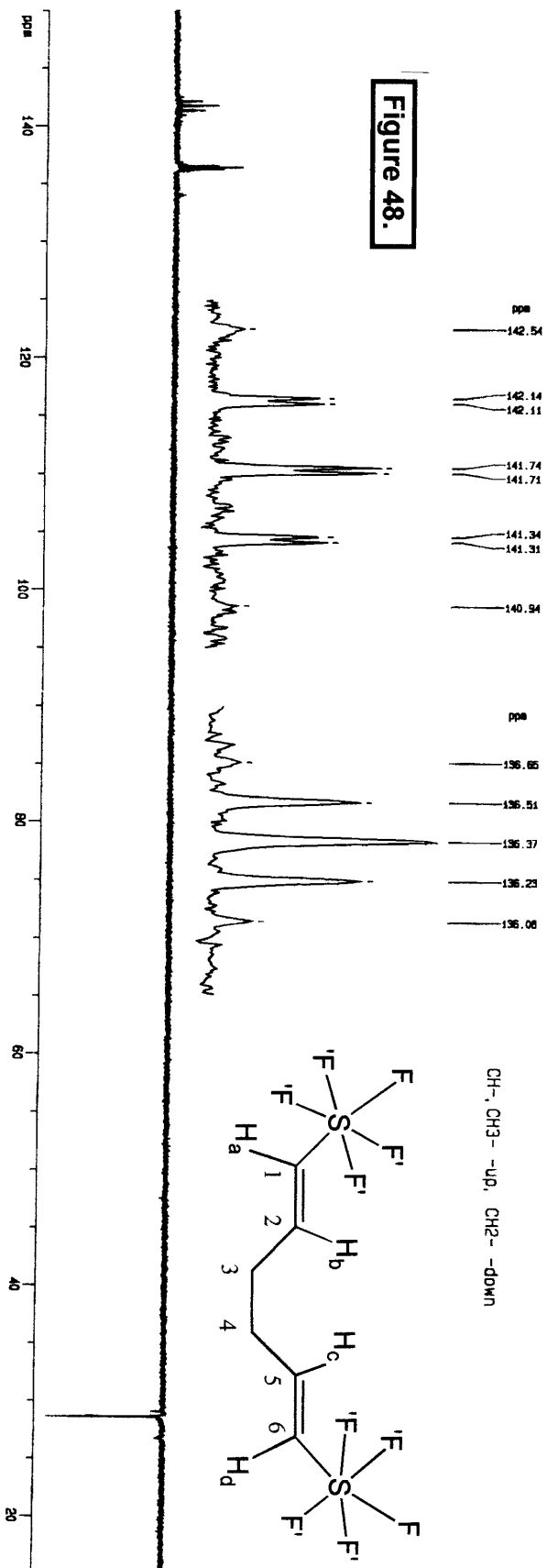


**Figure 46.**

188.31 MHz  $^{19}\text{F}$   
 $\text{F}-15$  ( $\text{CDCl}_3$ ), ref.  $\text{CF}_3\text{COOH}$

**Figure 47**





### 3.1.4. Experimental section.

NMR spectra were recorded on a Bruker CXP - 200 spectrometer at 200 MHz ( $^1\text{H}$  NMR), 188 MHz ( $^{19}\text{F}$  NMR) and 50.3 MHz ( $^{13}\text{C}$  NMR). Chemical shifts for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are referenced to the residual protons in the deuteriated solvent,  $^{19}\text{F}$  chemical shifts are given relatively to external  $\text{CF}_3\text{COOH}$ . Infrared spectra were recorded on a Bruker IFS-113 spectrometer. Samples were typically prepared as films or in  $\text{CCl}_4$  solution. Band frequencies ( $\nu$ ) are reported in ( $\text{cm}^{-1}$ ). Microanalyses were performed on a Carlo Erba instrument. Solvents were purified as follows were purified by literature procedures.

#### Synthesis of 2-Chloro-3-(pentafluoro-1<sup>6</sup>-sulfanyl)propan-1-ol (**6**) ( photochemical reaction).

A mixture of allyl alcohol (5.8 g, 0.1 mol), sulphur chloride pentafluoride (19.44g, 0.12 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation uv light with used of Hg-lamp (Type 60B A-36 quartz mercury atc lamp) in glass ampoule for 2.5 h at 10–15°C. Distillation of the liquid product gave 18.7g (83%) of **6**, b.p. 66–68°C at 3 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.2 (s, 1H, OH), 3.78 (m, 2H,  $\text{CH}_2\text{OH}$ ), 3.90 (m, 1H,  $\text{CH}_2\text{SF}_5$ ), 4.2 (m, 1H,  $\text{CH}_2\text{SF}_5$ ), 4.5 (m, 1H,  $\text{CHCl}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.6 (pent., 1F,  $J_{\text{F-F}}$  = 143.8 Hz), 142.2 (d, 4F,  $J_{\text{F-F}}$  = 143.8 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 56.44 (pent.,  $J_{\text{C-F}}$  = 4.4 Hz,  $\text{CCl}$ ), 65.12 (pent,  $J_{\text{C-F}}$  = 1.5 Hz,  $\text{CH}_2\text{OH}$ ), 72.72 (d.pent,  $J_{\text{C-F}}$  = 15.2 Hz,  $J_{\text{C-F}}$  = 0.9 Hz,  $\text{CH}_2\text{SF}_5$ ).

#### Synthesis of 3-Chloro-4-(pentafluoro-1<sup>6</sup>-sulfanyl)butane-1-ol (**7**) ( photochemical reaction).

Using the procedure for the synthesis of **6**, a mixture of 3-buten-1-ol (7.2 g, 0.1 mol), sulphur chloride pentafluoride (19.44g, 0.12 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation uv light. Yield 18.72 g (80%) **7**, b.p. 92 °C at 5 mm Hg.

$^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.88 (m, 1H,  $\text{CH}_2$ ), 2.1 (s, 1H, OH), 2.15 (m, 1H,  $\text{CH}_2$ ), 3.85 (m, 2H,  $\text{CH}_2\text{OH}$ ), 4.00 (m, 2H,  $\text{CH}_2\text{SF}_5$ ), 4.59 (m, 1H,  $\text{CHCl}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.9 (pent., 1F,  $J_{\text{F-F}}$  = 149.6 Hz), 144.0 (d, 4F,  $J_{\text{F-F}}$  = 149.6 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 39.54 (pent.,  $J_{\text{C-F}}$  = 1.2 Hz,  $\text{CH}_2$ ), 52.76 (pent.,  $J_{\text{C-F}}$  = 4.4 Hz,  $\text{CCl}$ ), 58.70 (s,  $\text{CH}_2\text{OH}$ ), 76.89 (d.pent.,  $J_{\text{C-F}}$  = 13.5 Hz,  $J_{\text{C-F}}$  = 0.9 Hz,  $\text{CH}_2\text{SF}_5$ ).

#### Synthesis of 4-Chloro-5-(pentafluoro-1<sup>6</sup>-sulfanyl)pentane-1-ol (**8**) ( photochemical reaction).

Using the procedure for the synthesis of **6**, a mixture of 4-penten-1-ol (8.6 g, 0.1 mol), sulphur chloride pentafluoride (19.44g, 0.12 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation uv light. Yield 20.8 g (84%) **8**, b.p. 102 °C at 2 mm Hg

$^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.91 (m, 4H, 2 $\text{CH}_2$ ), 2.0 (s, 1H, OH), 3.80 (m, 2H,  $\text{CH}_2\text{OH}$ ), 4.00 (m, 2H,  $\text{CH}_2\text{SF}_5$ ), 4.59 (m, 1H,  $\text{CHCl}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.6 (pent., 1F,  $J_{\text{F-F}}$  = 149.5 Hz), 144.1 (d, 4F,  $J_{\text{F-F}}$  = 149.8 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 32.0 (s,  $\text{CH}_2$ ), 36.34 (pent.,  $J_{\text{C-F}}$  = 1.1 Hz,  $\text{CH}_2$ ), 53.06 (pent.,  $J_{\text{C-F}}$  = 4.6 Hz,  $\text{CCl}$ ), 57.60 (s,  $\text{CH}_2\text{OH}$ ), 75.64 (d.pentet,  $J_{\text{C-F}}$  = 13.5 Hz,  $J_{\text{C-F}}$  = 1.0 Hz,  $\text{CH}_2\text{SF}_5$ ).

#### Synthesis of 3-Chloro-4-(pentafluoro-1<sup>6</sup>-sulfanyl)butane-2-ol (**9**) (photochemical reaction).

Using the procedure for the synthesis of **6**, a mixture of 3-buten-2-ol (7.2 g, 0.1 mol), sulphur chloride pentafluoride (19.44g, 0.12 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation uv light. Yield 19.4 g (83%) **9**, b.p. 93 °C at 12 mm Hg

$^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.38 (d, 3H,  $J_{\text{H-H}}$  = 6.0 Hz,  $\text{CH}_3$ ), 1.92 (br.s, 1H, OH), 4.03 (m, 2H,  $\text{CH}_2\text{SF}_5$ ), 4.16 (m, 1H,  $\text{CHOH}$ ), 4.52 (m, 1H,  $\text{CHCl}$ ) (a mixture of diastereomers);

$^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 161.0 (pent., 1F,  $J_{\text{F-F}}$  = 146.3 Hz), 160.8 (pent., 1F,  $J_{\text{F-F}}$  = 146.6 Hz), 144.2 (d, 4F,  $J_{\text{F-F}}$  = 146.3 Hz), 144.1 (d, 4F,  $J_{\text{F-F}}$  = 146.6 Hz) (a mixture of diastereomers);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 18.80 (s,  $\text{CH}_3$ ), 20.05 (s,  $\text{CH}_3$ ), 60.92 (pent.,  $J_{\text{C-F}}$  = 4.0 Hz,  $\text{CCl}$ ), 60.80 (pent.,  $J_{\text{C-F}}$  = 4.1 Hz,  $\text{CCl}$ ), 68.73 (s,  $\text{CHOH}$ ), 70.22 (s,  $\text{CH}$ , OH), 73.65 (d.pent.,  $J_{\text{C-F}}$  = 13.3 Hz,  $J_{\text{C-F}}$  = 0.9 Hz,  $\text{CH}_2\text{SF}_5$ ) 74.04 (d.pent.,  $J_{\text{C-F}}$  = 13.0 Hz,  $J_{\text{C-F}}$  = 1.0 Hz,  $\text{CH}_2\text{SF}_5$ ) (a mixture of diastereomers).

### Synthesis of 4-Chloro-5-(pentafluoro-1<sup>6</sup>-sulfanyl)pentane-2-ol (10) (photochemical reaction).

Using the procedure for the synthesis of 6, a mixture of 4-penten-2-ol (8.6 g, 0.1 mol), sulphur chloride pentafluoride (19.44g, 0.12 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation w light. Yield 21.1 g (85%) 7, b.p. 98 °C at 5 mm Hg.

$^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.24 (d, 3H,  $J_{\text{H-H}}$  = 6.2 Hz,  $\text{CH}_3$ ), 1.84 (m, 2H,  $\text{CH}_2$ ), 1.95 (br.s, 1H, OH), 4.02 (m, 2H,  $\text{CH}_2\text{SF}_5$ ), 4.12 (m, 1H,  $\text{CHOH}$ ), 4.52 (m, 1H,  $\text{CHCl}$ ) (a mixture of diastereomers);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 161.13 (pent., 1F,  $J_{\text{F-F}}$  = 149.0 Hz), 161.04 (pent., 1F,  $J_{\text{F-F}}$  = 149.3 Hz), 144.29 (d, 4F,  $J_{\text{F-F}}$  = 149.3 Hz), 143.8 (d, 4F,  $J_{\text{F-F}}$  = 149.0 Hz) (a mixture of diastereomers);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 23.10 (s,  $\text{CH}_3$ ), 23.83 (s,  $\text{CH}_3$ ), 45.74 (s,  $\text{CH}_2$ ), 46.13 (s,  $\text{CH}_2$ ), 52.99 (pent.,  $J_{\text{C-F}}$  = 4.0 Hz,  $\text{CCl}$ ), 53.07 (pent.,  $J_{\text{C-F}}$  = 4.0 Hz,  $\text{CCl}$ ), 64.40 (s,  $\text{CHOH}$ ), 65.08 (s,  $\text{CHOH}$ ), 76.80 (d.pent.,  $J_{\text{C-F}}$  = 13.4 Hz,  $J_{\text{C-F}}$  = 0.9 Hz,  $\text{CH}_2\text{SF}_5$ ) 77.02 (d.pent.,  $J_{\text{C-F}}$  = 13.3 Hz,  $J_{\text{C-F}}$  = 0.9 Hz,  $\text{CH}_2\text{SF}_5$ ) (a mixture of diastereomers).

### Synthesis of 2-Chloro-3-(pentafluoro-1<sup>6</sup>-sulfanyl)propane-1-ol (6) (autoclave reaction).

Into a 150 ml Hoke stainless steel reaction vessel was added of allyl alcohol (5.8 g, 0.1 mol). The vessel was then cooled to  $-196^\circ\text{C}$ , evacuated and warmed to room temperature. This freeze-thaw process was repeated twice more to remove air from the vessel. After cooling to  $-196^\circ\text{C}$ , 19.44g (0.12 mol) sulphur chloride pentafluoride was condensed into the vessel and then heated at  $60^\circ\text{C}$  for 48 h. Distillation at reduced pressure provided 4.4 g (20% yield) of 6.

### Synthesis of 3-Chloro-4-(pentafluoro-1<sup>6</sup>-sulfanyl)butane-1-ol (7) (autoclave reaction).

Using the procedure for the synthesis of 6 (autoclave reaction), a mixture of 3-buten-1-ol (7.2 g, 0.1 mol) and sulphur chloride pentafluoride (19.44g, 0.12 mol) was heated at  $60^\circ\text{C}$  for 48 h. in autoclave. Yield: 23% (7).

### Synthesis of 4-Chloro-5-(pentafluoro-1<sup>6</sup>-sulfanyl)pentane-1-ol (8) (autoclave reaction).

Using the procedure for the synthesis of 6 (autoclave reaction), a mixture of 4-penten-1-ol (8.6 g, 0.1 mol) and sulphur chloride pentafluoride (19.44g, 0.12 mol) was heated at  $60^\circ\text{C}$  for 48 h. in autoclave. Yield: 27% (8).

### Synthesis of 3-Chloro-4-(pentafluoro-1<sup>6</sup>-sulfanyl)butane-2-ol (9) (autoclave reaction).

Using the procedure for the synthesis of 6 (autoclave reaction), a mixture of 3-buten-2-ol (7.2 g, 0.1 mol) and sulphur chloride pentafluoride (19.44g, 0.12 mol) was heated at  $60^\circ\text{C}$  for 48 h. in autoclave. Yield: 21% (9).

### Synthesis of 4-Chloro-5-(pentafluoro-1<sup>6</sup>-sulfanyl)pentane-2-ol (10) (autoclave reaction).

Using the procedure for the synthesis of 6 (autoclave reaction), a mixture of 4-penten-2-ol (8.6 g, 0.1 mol) and sulphur chloride pentafluoride (19.44g, 0.12 mol) was heated at  $60^\circ\text{C}$  for 48 h. in autoclave. Yield: 23% (10).

### Synthesis of 3-(pentafluoro- $\lambda^6$ -sulfanyl)prop-2-en-1-ol (**11**).

A mixture of potassium hydroxide (6 g), 2-chloro-3-(pentafluoro- $\lambda^6$ -sulfanyl)propane-1-ol (6.6 g, 0.03 mol) and 50 ml diethyl ether was stirred at 30-40°C for 1.5 h, and then to mixture was added 100 ml of water. The two layers were separated and the aqueous phase was extracted with Et<sub>2</sub>O (3 × 30mL). The combined organic fractions were dried (MgSO<sub>4</sub>) and solvent was evaporated in vacuum. Distillation of the crude 3-(pentafluoro- $\lambda^6$ -sulfanyl)prop-2-en-1-ol gave 3.6g (65%) of **11**, b.p. 73-74 °C at 15 mm Hg. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 2.25 (br.s, 1H, OH), 4.37 (m, 2H,  $\underline{\text{CH}_2\text{OH}}$ ), 6.7 (m, 2H, F<sub>5</sub>SCH=CH); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 161.3 (pent., 1F, J<sub>F-F</sub> = 150.3 Hz). 141.0 (d, 4F, J<sub>F-F</sub> = 150.3 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 59.97 (s, CH<sub>2</sub>OH), 137.36 (pent., J<sub>C-F</sub> = 6.9 Hz, =CH), 140.2 (d.pent., J<sub>C-F</sub> = 15.6 Hz, J<sub>C-F</sub> = 1.6 Hz, =CHSF<sub>5</sub>).

### Synthesis of 4-(pentafluoro- $\lambda^6$ -sulfanyl)but-3-en-1-ol (**12**).

Using the procedure for the synthesis of **11**, a mixture of potassium hydroxide (6 g), 3-chloro-4-(pentafluoro- $\lambda^6$ -sulfanyl)butan-1-ol (7.0 g, 0.03 mol) and 50 ml diethyl ether was stirred at 30-40°C for 1.5 h. b.p. 64-65 °C at 1.5 mm Hg, yield of **12** 3.9 g (66%). <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 2.35 (br.s, 1H, OH), 2.4 (m, 2H, CH<sub>2</sub>), 3.72 (t, 2H, J<sub>H-H</sub> = 5.0 Hz,  $\underline{\text{CH}_2\text{OH}}$ ), 6.5 (m, 2H, F<sub>5</sub>SCH=CH); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 161.6 (pent., 1F, J<sub>F-F</sub> = 152.8 Hz). 140.2 (d, 4F, J<sub>F-F</sub> = 152.8 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 33.38 (s, CH<sub>2</sub>), 60.36 (pent., J<sub>C-F</sub> = 1.0 Hz, CH<sub>2</sub>OH), 135.64 (pent., J<sub>C-F</sub> = 7.1 Hz, =CH), 142.0 (d.pent., J<sub>C-F</sub> = 19.5 Hz, J<sub>C-F</sub> = 1.6 Hz, =CHSF<sub>5</sub>).

### Synthesis of 5-(pentafluoro- $\lambda^6$ -sulfanyl)pent-4-en-1-ol (**13**).

Using the procedure for the synthesis of **11**, a mixture of potassium hydroxide (6 g), 4-chloro-5-(pentafluoro- $\lambda^6$ -sulfanyl)pentane-1-ol (7.4 g, 0.03 mol) and 50 ml diethyl ether was stirred at 30-40°C for 1.5 h. b.p. 72-73 °C at 1.5 mm, yield of **13** 4.4 g (69%). <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.9 (m, 4H, 2 CH<sub>2</sub>), 2.35 (br.s, 1H, OH), 3.11 (t, 2H, J<sub>H-H</sub> = 5.1 Hz,  $\underline{\text{CH}_2\text{OH}}$ ), 6.5 (m, 2H, F<sub>5</sub>SCH=CH); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 161.8 (pent., 1F, J<sub>F-F</sub> = 152.0 Hz). 140.4 (d, 4F, J<sub>F-F</sub> = 152.1 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 28.1 (s, CH<sub>2</sub>), 33.38 (pent., J<sub>C-F</sub> = 1.0 Hz, CH<sub>2</sub>), 62.30 (s, CH<sub>2</sub>OH), 135.64 (pent., J<sub>C-F</sub> = 7.1 Hz, =CH), 142.0 (d.pent., J<sub>C-F</sub> = 19.5 Hz, J<sub>C-F</sub> = 1.6 Hz, =CHSF<sub>5</sub>).

### Synthesis of 4-(pentafluoro- $\lambda^6$ -sulfanyl)but-3-en-2-ol (**14**).

Using the procedure for the synthesis of **11**, a mixture of potassium hydroxide (6 g), 3-chloro-4-(pentafluoro- $\lambda^6$ -sulfanyl)butan-2-ol (7.0 g, 0.03 mol) and 50 ml diethyl ether was stirred at 30-40°C for 1.5 h. b.p. 76-77 °C at 12 mm, yield of **14** 3.5 g (60%). <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.39 (d, 3H, J<sub>H-H</sub> = 6.6 Hz, CH<sub>3</sub>), 1.91 (br.s, 1H, OH), 4.53 (m, 1H, J<sub>H-H</sub> = 6.6 Hz, J<sub>H-H</sub> = 4.4 Hz,  $\underline{\text{CHOH}}$ ), 6.53 (m, 1H, J<sub>H-H</sub> = 4.4 Hz, J<sub>H-H</sub> = 14.5 Hz, J<sub>H-F</sub> = 1.1 Hz, =CH), 6.68 (m, 1H, J<sub>H-H</sub> = 14.5 Hz, J<sub>H-F</sub> = 6.5 Hz, =CHSF<sub>5</sub>); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 161.3 (pent., 1F, J<sub>F-F</sub> = 153.2 Hz), 141.1 (d, 4F, J<sub>F-F</sub> = 153.2 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 22.61 (s, CH<sub>3</sub>), 65.86 (s, CHOH), 139.90 (pent., J<sub>C-F</sub> = 19.0 Hz, J<sub>C-F</sub> = 1.5 Hz, =CHSF<sub>5</sub>), 141.4 (d.pent., J<sub>C-F</sub> = 6.6 Hz, =CH).

### Synthesis of 5-(pentafluoro- $\lambda^6$ -sulfanyl)pent-4-en-2-ol (**15**).

Using the procedure for the synthesis of **11**, a mixture of potassium hydroxide (6 g), 4-chloro-5-(pentafluoro- $\lambda^6$ -sulfanyl)pentan-2-ol (7.4 g, 0.03 mol) and 50 ml diethyl ether was stirred at 30–40°C for 1.5 h. b.p. 84 °C at 1.5 mm, yield of **15** 4.3 g (67%). <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.2 (d, 3H,  $J_{H-H}$  = 6.2 Hz, CH<sub>3</sub>), 1.9 (s, 1H, OH), 2.29 (m, CH<sub>2</sub>), 3.93 (m, 1H, CHOH), 6.52 (m, 2H, F<sub>3</sub>SCH=CH); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 161.6 (pent., 1F,  $J_{F-F}$  = 152.7 Hz), 140.3 (d, 4F,  $J_{F-F}$  = 152.7 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 23.11 (s, CH<sub>3</sub>), 39.62 (s, CH<sub>2</sub>), 66.32 (s, CHOH), 135.37 (pent.,  $J_{C-F}$  = 7.2 Hz, =CH), 142.0 (d.pent.,  $J_{C-F}$  = 19.5 Hz,  $J_{C-F}$  = 1.7 Hz, =CHSF<sub>5</sub>).

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopropane (**19**) (photochemical reaction).

A mixture of methylenecyclopropane (2.7 g, 0.05 mol), sulphur chloride pentafluoride (8.5g, 0.052 mol) and CF<sub>3</sub>Cl (10 ml) was irradiation ultra-violet light with used of Hg-lamp (Type 60B A-36 quartz mercury atc lamp) in glass ampoule for 2 h at 0–5°C. Distillation of the liquid product gave 10.1g (94%) of **6**, b.p. 60 °C at 25 mm Hg. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.3 (m, 4H, 2CH<sub>2</sub>), 3.89 (pent. 2H,  $J_{H-F}$  = 8.0 Hz, CH<sub>2</sub>SF<sub>5</sub>); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 160.9 (pent., 1F,  $J_{F-F}$  = 149.6 Hz), 144.0 (d, 4F,  $J_{F-F}$  = 149.6 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 18.28 (pent.  $J_{C-F}$  = 1.0 Hz, CH<sub>2</sub>), 36.97 (pent.  $J_{C-F}$  = 3.7 Hz, CCl), 80.91 (d.pent.,  $J_{C-F}$  = 13.7 Hz,  $J_{C-F}$  = 1.7 Hz, CH<sub>2</sub>SF<sub>5</sub>).

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclobutane (**20**) (photochemical reaction).

Using the procedure for the synthesis of **19**, a mixture of methylenecyclobutane (3.4 g, 0.05 mol), sulphur chloride pentafluoride (8.5g, 0.052 mol) and CF<sub>3</sub>Cl (10 ml) was irradiation ultra-violet lamp. Yield 8.72 g (91%) **20**, b.p. 57°C at 15 mm Hg. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 2.3 (m, 2H, CH<sub>2</sub>), 2.61 (m, 4H, 2CH<sub>2</sub>), 4.00 (pent. 2H,  $J_{H-F}$  = 8.8 Hz CH<sub>2</sub>SF<sub>5</sub>); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 160.7 (pent., 1F,  $J_{F-F}$  = 150.5 Hz), 144.0 (d, 4F,  $J_{F-F}$  = 150.5 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 14.96 (s, CH<sub>2</sub>), 38.06 (pent.  $J_{C-F}$  = 1.7 Hz, 2CH<sub>2</sub>), 63.93 (pent.  $J_{C-F}$  = 2.9 Hz, CCl), 79.19 (d.pent.,  $J_{C-F}$  = 13.1 Hz,  $J_{C-F}$  = 1.7 Hz, CH<sub>2</sub>SF<sub>5</sub>).

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopentane (**21**) (photochemical reaction).

Using the procedure for the synthesis of **19**, a mixture of methylenecyclopentane (4.1 g, 0.05 mol), sulphur chloride pentafluoride (8.5g, 0.052 mol) and CF<sub>3</sub>Cl (10 ml) was irradiation ultra-violet lamp. Yield 8.72 g (93%) **21**, b.p. 66°C at 15 mm Hg. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 2.1–2.3 (m, 4H, 2CH<sub>2</sub>), 2.59 (m, 4H, 2CH<sub>2</sub>), 4.04 (pent., 2H,  $J_{H-F}$  = 8.8 Hz CH<sub>2</sub>SF<sub>5</sub>); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 160.6 (pent., 1F,  $J_{F-F}$  = 150.0 Hz), 144.1 (d, 4F,  $J_{F-F}$  = 150. Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 14.01 (s, 2CH<sub>2</sub>), 36.15 (pent.  $J_{C-F}$  = 1.6 Hz, 2CH<sub>2</sub>), 60.64 (pent.  $J_{C-F}$  = 2.9 Hz, CCl), 78.85 (d.pent.,  $J_{C-F}$  = 13.0 Hz,  $J_{C-F}$  = 1.7 Hz, CH<sub>2</sub>SF<sub>5</sub>).

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopropane (**19**) (autoclave reaction).

Into a 50 ml Hoke stainless steel reaction vessel was added of methylenecyclopropane (2.7 g, 0.05 mol). The vessel was then cooled to -196°C, evacuated and warmed to room temperature. This freeze-thaw process was repeated twice more to remove air from the vessel. After cooling to -196°C, sulphur chloride pentafluoride (8.5g, 0.052 mol) was condensed into the vessel and then heated at 60°C for 24 h. Distillation at reduced pressure provided 8.1 g (75% yield) of **19**.

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclobutane (**20**) (autoclave reaction).



Using the procedure for the synthesis of **19** (autoclave reaction), a mixture of methylenecyclobutane (3.4 g, 0.05 mol) and sulphur chloride pentafluoride (8.5g, 0.052 mol) was heated at 60<sup>0</sup>C for 24 h in autoclave. Yield of **20** 9.2 g (80%).

#### Synthesis of 1-Chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopentane (**21**) (autoclave reaction).

Using the procedure for the synthesis of **19** (autoclave reaction), a mixture of methylenecyclopentane (4.1 g, 0.05 mol) and sulphur chloride pentafluoride (8.5g, 0.052 mol) was heated at 60<sup>0</sup>C for 24 h in autoclave. Yield of **21** 9.3 g (76 %).

#### Synthesis of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclopropane (**22**).

A mixture of potassium carbonate (7 g), 1-chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopropane (5.4 g, 0.025 mol) and 30 ml tetramethylene sulfone (sulfolane) was stirred at 65-70<sup>0</sup>C for 4.5 h. After cooling to room temperature and filtration the crude product was removed from reaction mixture into a trap (cooling at -70<sup>0</sup>C) at 30-40<sup>0</sup>C/1-2 mm Hg. Redistillation gives 3.2g (71%) of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclopropane, b.p. 106-108 <sup>0</sup>C. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.5 (m, 4H, 2CH<sub>2</sub>), 6.8 (m, 2H, CH=); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 160.9 (pent., 1F, J<sub>F-F</sub> = 146.8 Hz), 140.1 (d, 4F, J<sub>F-F</sub> = 146.8 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 5.03 (pent. J<sub>C-F</sub> = 0.9 Hz, CH<sub>2</sub>), 6.49 (s, CH<sub>2</sub>), 131.03 (d, pent. J<sub>C-F</sub> = 20.0 Hz, J<sub>C-F</sub> = 1.7 Hz, =CHSF<sub>5</sub>), 132.2 (pent. J<sub>C-F</sub> = 7.3 Hz, =C)

#### Synthesis of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclobutane (**23**).

A mixture of potassium hydroxide (3 g), 1-chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclobutane (5.8 g, 0.025 mol) and 30 ml tetrahydrofuran was stirred at 65<sup>0</sup>C for 7 h, and then to mixture was added 50 ml of water. The two layers were separated and the aqueous phase was extracted with Et<sub>2</sub>O (3  $\times$  30mL). The combined organic fractions were dried (MgSO<sub>4</sub>) and solvent was evaporated in vacuum. Distillation of the crude product gives 3.2g (65%) of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclobutane, b.p. 126-128 <sup>0</sup>C. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 2.06 (pent., 2H, J<sub>H-H</sub> = 8.0 Hz, CH<sub>2</sub>), 2.82 (m, 2H, CH<sub>2</sub>), 3.03 (m, 2H, CH<sub>2</sub>), 6.2 (pent.pent. J<sub>H-F</sub> = 2.2 Hz, J<sub>H-H</sub> = 2.3 Hz, 1H, CH=); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 163.2 (pent, 1F, J<sub>F-F</sub> = 150.6 Hz), 142.6 (d, 4F, J<sub>F-F</sub> = 150.6 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 16.29 (pent. J<sub>C-F</sub> = 1.5 Hz, CH<sub>2</sub>), 29.75 (pent. J<sub>C-F</sub> = 0.7 Hz, CH<sub>2</sub>), 31.98 (pent. J<sub>C-F</sub> = 1.2 Hz, CH<sub>2</sub>), 132.08 (d.pent., J<sub>C-F</sub> = 18.8 Hz, J<sub>C-F</sub> = 1.6 Hz, =CHSF<sub>5</sub>), 152.8 (pent, J<sub>C-F</sub> = 6.5 Hz, =C).

#### Synthesis of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclopropene (**24**).

Using the procedure for the synthesis of **23**, a mixture of potassium hydroxide (3 g), 1-chloro-1-[(pentafluoro- $\lambda^6$ -sulfanyl)methyl]cyclopentane (6.1 g, 0.025 mol) and 30 ml tetrahydrofuran was stirred at 65<sup>0</sup>C for 7.0 h. Distillation gives 3.3g (64%) of [(pentafluoro- $\lambda^6$ -sulfanyl)methylene]cyclopentane, b.p. 140-142 <sup>0</sup>C. <sup>1</sup>H NMR (200 MHz, TMS, CDCl<sub>3</sub>):  $\delta$  = 1.84 (m, 4H, 2CH<sub>2</sub>), 2.52 (m, 2H, CH<sub>2</sub>), 2.81 (m, 2H, CH<sub>2</sub>), 6.01 (pent.pent. J<sub>H-F</sub> = 2.0 Hz, J<sub>H-H</sub> = 3.1 Hz, 1H, CH=); <sup>19</sup>F NMR (188 MHz, CF<sub>3</sub>COOH, CDCl<sub>3</sub>):  $\delta$  = 163.1 (pent, 1F, J<sub>F-F</sub> = 151.2 Hz), 142.8 (d, 4F, J<sub>F-F</sub> = 151.2 Hz); <sup>13</sup>C NMR (50.3 MHz, TMC, CDCl<sub>3</sub>): 12.31 (s, CH<sub>2</sub>), 12.35 (s, CH<sub>2</sub>), 27.23 (s, CH<sub>2</sub>), 29.08 (pent., J<sub>C-F</sub> = 1.3 Hz, CH<sub>2</sub>), 131.12 (d.pent., J<sub>C-F</sub> = 19.1 Hz, J<sub>C-F</sub> = 1.4 Hz, =CHSF<sub>5</sub>), 137.2 (pent, J<sub>C-F</sub> = 7.2 Hz, =C).

#### Synthesis of 4-chloro-5-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1-en (**25**).

A mixture of 1,4-pentadiene (4.1 g, 0.06 mol), sulphur chloride pentafluoride (8.1g, 0.05 mol) and  $\text{CF}_3\text{Cl}$  (10 ml) was irradiation ultra-violet light with used of Hg-lamp (Type 60B A-36 quartz mercury atc lamp) in glass ampoule for 2 h at 5–10°C. Distillation of the liquid product gave 10 g (87%) of **25**, b.p. 51 °C at 12 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.63 (m, 2H, =CH-CH<sub>2</sub>), 3.95 (d.pent. 2H,  $J_{\text{H-H}}$  = 9.5 Hz,  $J_{\text{H-F}}$  = 8.0 Hz,  $\text{CH}_2\text{SF}_5$ ), 4.43 (m, 1H,  $\text{CHCl}$ ), 5.18 (1H,  $J_{\text{H-H}}$  = 10.1 Hz,  $J_{\text{H-H}}$  = 1.0 Hz, CH=), 5.22 (1H,  $J_{\text{H-H}}$  = 16.3 Hz,  $J_{\text{H-H}}$  = 1.0 Hz, CH=), 5.82 (m, 1H, CH=);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.6 (pent., 1F,  $J_{\text{F-F}}$  = 150.2 Hz), 144.0 (d, 4F,  $J_{\text{F-F}}$  = 150.2 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 41.38 (pent.,  $J_{\text{C-F}}$  = 1.2 Hz.,  $\text{CH}_2$ ), 54.26 (pent.  $J_{\text{C-F}}$  = 4.2 Hz,  $\text{CCl}$ ), 75.74 (d.pent.,  $J_{\text{C-F}}$  = 13.4 Hz,  $J_{\text{C-F}}$  = 0.9 Hz  $\text{CH}_2\text{SF}_5$ ), 120.04 (s,  $\text{CH}_2$ ), 131.62 (s, =CH).

#### Synthesis of 5-chloro-6-(pentafluoro-1<sup>6</sup>-sulfanyl)hex-1-en (**26**).

Using the procedure for the synthesis of **25**, a mixture of 1,6-hexadiene (4.9 g, 0.06 mol), sulphur chloride pentafluoride (8.1g, 0.05 mol) and  $\text{CF}_3\text{Cl}$  (10 ml) was irradiation ultra-violet lamp. Yield 11.3 g (93%) **26**, b.p. 64°C at 12 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.84 (m, 1H, -CHH), 2.00 (m, 1H, -CHH), 2.3 (m, 2H, =CH-CH<sub>2</sub>), 4.0 (m, 2H,  $\text{CH}_2\text{SF}_5$ ), 4.4 (m, 1H,  $\text{CHCl}$ ), 5.09 (1H,  $J_{\text{H-H}}$  = 9.5 Hz,  $J_{\text{H-H}}$  = 1.0 Hz, CH=), 5.12 (1H,  $J_{\text{H-H}}$  = 16.3 Hz,  $J_{\text{H-H}}$  = 1.0 Hz, CH=), 5.74 (m, 1H, CH=);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.9 (pent., 1F,  $J_{\text{F-F}}$  = 149.1 Hz), 142.6 (d, 4F,  $J_{\text{F-F}}$  = 149.1 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 30.05 (s,  $\text{CH}_2$ ), 36.45 (pent.,  $J_{\text{C-F}}$  = 1.2 Hz,  $\text{CH}_2$ ), 54.92 (pent.  $J_{\text{C-F}}$  = 4.4 Hz,  $\text{CCl}$ ), 76.72 (d.pent.,  $J_{\text{C-F}}$  = 13.3 Hz,  $J_{\text{C-F}}$  = 0.9 Hz  $\text{CH}_2\text{SF}_5$ ), 116.57 (s, =CH<sub>2</sub>), 135.82 (s, =CH).

#### Synthesis of 2,4-dichloro-1,5-di(pentafluoro-1<sup>6</sup>-sulfanyl)pentane (**27**).

Using the procedure for the synthesis of **25**, a mixture of 1,5-pentadiene (3.4 g, 0.05 mol), sulphur chloride pentafluoride (17.8 g, 0.11 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation ultra-violet lamp. Yield 15.5 g (79%) **27**, b.p. 102°C at 5 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.31 (d.d., 2H,  $J_{\text{H-H}}$  = 7.6 Hz,  $J_{\text{H-H}}$  = 7.5 Hz,  $\text{CH}_2$ ), 4.0 (m, 4H, 2 $\text{CH}_2\text{SF}_5$ ), 4.68 (m, 2H, 2 $\text{CHCl}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.0 (pent., 1F,  $J_{\text{F-F}}$  = 149.7 Hz), 144.9 (d, 4F,  $J_{\text{F-F}}$  = 149.7 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 44.5 (pent.,  $J_{\text{C-F}}$  = 1.2 Hz,  $\text{CH}_2$ ), 52.44 (pent.  $J_{\text{C-F}}$  = 4.8 Hz,  $\text{CCl}$ ), 76.76 (d.pent.,  $J_{\text{C-F}}$  = 14.0 Hz,  $J_{\text{C-F}}$  = 1.0 Hz  $\text{CH}_2\text{SF}_5$ ).

#### Synthesis of 2,5-dichloro-1,6-di(pentafluoro-1<sup>6</sup>-sulfanyl)hexane (**28**).

Using the procedure for the synthesis of **25**, a mixture of 1,6-hexadiene (4.1 g, 0.05 mol), sulphur chloride pentafluoride (17.8 g, 0.11 mol) and  $\text{CF}_3\text{Cl}$  (20 ml) was irradiation ultra-violet lamp. Yield 16.4 g (81%) **28**, b.p. 101°C at 2 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 1.84-2.32 (m, 4H, 2 $\text{CH}_2$ ), 4.0 (m, 4H, 2 $\text{CH}_2\text{SF}_5$ ), 4.38 (m, 2H, 2 $\text{CHCl}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta$  = 160.5 (pent., 1F,  $J_{\text{F-F}}$  = 148.9 Hz), 142.4 (d, 4F,  $J_{\text{F-F}}$  = 148.8 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 33.73 (pent., 1.2 Hz,  $\text{CH}_2$ ), 34.19 (pent., 1.2 Hz,  $\text{CH}_2$ ), 54.35 (pent.,  $J_{\text{C-F}}$  = 4.6 Hz,  $\text{CH}_2$ ), 54.98 (pent.  $J_{\text{C-F}}$  = 4.6 Hz,  $\text{CCl}$ ), 76.21 (d.pent.,  $J_{\text{C-F}}$  = 13.3 Hz,  $J_{\text{C-F}}$  = 0.9 Hz  $\text{CH}_2\text{SF}_5$ ), 76.30 (d.pent.,  $J_{\text{C-F}}$  = 13.3 Hz,  $J_{\text{C-F}}$  = 0.9 Hz  $\text{CH}_2\text{SF}_5$ ).

#### Synthesis of 1-(pentafluoro-1<sup>6</sup>-sulfanyl)penta-1,4-diene (**29**).

A mixture of potassium carbonate (6 g), 4-chloro-5-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1-ene (4.6 g, 0.02 mol) and 25 ml tetramethylene sulfone (sulfolane) was stirred at 65-70°C for 4.5 h. After cooling to room temperature and filtration the crude product was removed from reaction mixture into a trap (cooling at -70°C) at 30-40°C/1-2 mm Hg. Redistillation gives 2.3g (51%) of 1-(pentafluoro- $\lambda^6$ -sulfanyl)penta-1,4-diene, b.p. 61-63 °C at 40 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.96 (m, H,  $\text{CH}_2$ ), 5.17 (1H,  $J_{\text{H-H}}$  = 16.0 Hz,  $J_{\text{H-H}}$  = 1.0 Hz, CH=), 5.22 (1H,  $J_{\text{H-H}}$

$_{\text{H}} = 9.0$  Hz,  $J_{\text{H-H}} = 1.0$  Hz, CH=), 5.82 (m, 1H, CH=); 6.58 (m, 2H,  $\text{CH}_2\text{SF}_5$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta = 161.7$  (pent., 1F,  $J_{\text{F-F}} = 152.2$  Hz), 140.6 (d, 4F,  $J_{\text{F-F}} = 152.2$  Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 34.16 (pent.  $J_{\text{C-F}} = 0.9$  Hz,  $\text{CH}_2$ ), 118.21 (s,  $=\text{CH}_2$ ), 132.60 (s, CH=), 136.83 (pent.,  $J_{\text{C-F}} = 7.0$  Hz,  $=\text{C}$ ), 141.30 (d.pent.,  $J_{\text{C-F}} = 19.6$  Hz,  $J_{\text{C-F}} = 1.5$  Hz,  $=\text{CHSF}_5$ ).

### Synthesis of 1-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (30).

In a 20 ml reaction flask, 2.0 g (0.01 mol) of 5-(pentafluoro- $\lambda^6$ -sulfanyl)pent-4-en-2-ol (**15**) and 1 g of  $\text{H}_2\text{SO}_4$  are mixed, giving slight evolution of heat, and the reaction mixture is heated to 60–65  $^\circ\text{C}$ . The pressure is reduced to 25 mm Hg and the crude product was removed from reaction mixture into a trap (cooling at  $-70^\circ\text{C}$ ). Redistillation gives 0.58 (30%) of 1-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene, b.p. 52–54  $^\circ\text{C}$  at 100 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta = 1.85$  (d, 3H,  $J_{\text{H-H}} = 4.6$  Hz,  $\text{CH}_3$ ), 5.96 (m, CH=), 6.10 (m, 1H, CH=), 6.52 (m, 1H,  $=\text{CHSF}_5$ ), 6.83–7.2 (m, 1H,  $\text{CH}=\text{CHSF}_5$ ) (mixture of isomers);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta = 162.6$  (pent., 1F,  $J_{\text{F-F}} = 154.4$  Hz), 162.3 (pent., 1F,  $J_{\text{F-F}} = 155.6$  Hz), 141.96 (d, 4F,  $J_{\text{F-F}} = 154.4$  Hz), 142.20 (d, 4F,  $J_{\text{F-F}} = 155.6$  Hz) (mixture of isomers);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 13.75 (s,  $\text{CH}_3$ ), 18.46 (s,  $\text{CH}_3$ ), 123.65 (s,  $\text{CH}_3\text{CH}=\text{CH}$ ), 125.92 (s,  $\text{CH}_3\text{CH}=\text{CH}$ ), 130.98 (pent.,  $J_{\text{C-F}} = 7.4$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 136.52 (pent.,  $J_{\text{C-F}} = 1.7$  Hz,  $\text{CH}_3\text{CH}=\text{CH}$ ), 136.58 (pent.,  $J_{\text{C-F}} = 7.6$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 139.13 (d.pent.,  $J_{\text{C-F}} = 19.9$  Hz,  $J_{\text{C-F}} = 1.5$  Hz,  $=\text{CHSF}_5$ ), 139.99 (pent.,  $J_{\text{C-F}} = 1.6$  Hz,  $\text{CH}_3\text{CH}=\text{CH}$ ), 162.3 (d.pent.,  $J_{\text{C-F}} = 20.0$  Hz,  $J_{\text{C-F}} = 1.6$  Hz,  $=\text{CHSF}_5$ ).

### Synthesis of 1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (31) and 5-chloro-1-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (32).

A mixture of potassium carbonate (5 g), 2,4-dichloro-1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)pentane (3.9 g, 0.01 mol) and 15 ml DMF was stirred at 70–75  $^\circ\text{C}$  for 4.5 h. After cooling to room temperature and filtration, the DMF was removed from reaction mixture into a trap (cooling at  $-70^\circ\text{C}$ ) at 30–40  $^\circ\text{C}$ /1–2 mm Hg. The crude product was distillation at 60–70  $^\circ\text{C}$  at 1.5 mm Hg. The 1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (**31**) and 5-chloro-1-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (**32**) were isolated as stable colorless oils by column chromatography on silica gel (hexane: $\text{CHCl}_3 = 10:1$ ).

**1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (31).**  $R_f = 0.54$  (hexane: $\text{CHCl}_3 = 10:1$ ), Yield 1.6 g (50%).  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta = 4.37$  (d.pent., 2H,  $J_{\text{H-H}} = 7.5$  Hz,  $J_{\text{H-F}} = 7.0$  Hz,  $\text{CH}_2\text{SF}_5$ ), 6.25 (m, 2H,  $\text{CH}=\text{CH}-\text{CH}_2\text{SF}_5$ ), 6.62 (d.pent., 1H, m,  $J_{\text{H-H}} = 14.5$  Hz,  $J_{\text{H-F}} = 6.4$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 6.91 (d.d.  $J_{\text{H-H}} = 9.8$  Hz,  $J_{\text{H-H}} = 14.5$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta = 160.37$  (pent., 1F,  $J_{\text{F-F}} = 154.0$  Hz), 158.88 (pent., 1F,  $J_{\text{F-F}} = 155.7$  Hz), 142.85 (pent., 4F,  $J_{\text{F-F}} = 154.0$  Hz), 141.2 (pent., 4F,  $J_{\text{F-F}} = 155.7$  Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 72.49 (d.pent.,  $J_{\text{C-F}} = 15.6$  Hz,  $J_{\text{C-F}} = 0.9$  Hz,  $\text{F}_5\text{SCH}_2$ ), 129.30 (m, CH=), 132.55 (pent.,  $J_{\text{C-F}} = 1.3$  Hz,  $=\text{CH}$ ), 134.21 (pent.,  $J_{\text{C-F}} = 7.6$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 143.64 (d.pent.,  $J_{\text{C-F}} = 20.0$  Hz,  $J_{\text{C-F}} = 1.5$  Hz,  $=\text{CHSF}_5$ ).

**5-chloro-1-(pentafluoro- $\lambda^6$ -sulfanyl)pent-1,3-diene (32).**  $R_f = 0.66$  (hexane:  $\text{CHCl}_3 = 10:1$ ), Yield 0.46 g (20%).  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta = 4.14$  (d, 2H,  $J_{\text{H-H}} = 4.1$  Hz,  $\text{CH}_2\text{Cl}$ ), 6.23 (m, 2H,  $\text{CH}=\text{CH}$ ), 6.6 (d.pent., 1H,  $J_{\text{H-H}} = 14.34$  Hz,  $J_{\text{H-F}} = 6.5$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 6.88 (d.d.pent.,  $J_{\text{H-H}} = 8.5$  Hz,  $J_{\text{H-H}} = 14.5$  Hz,  $J_{\text{H-F}} = 1.4$  Hz, 1H,  $\text{CH}=\text{CHSF}_5$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CF}_3\text{COOH}$ ,  $\text{CDCl}_3$ ):  $\delta = 161.2$  (pent., 1F,  $J_{\text{F-F}} = 148.8$  Hz), 141.45 (d, 4F,  $J_{\text{F-F}} = 148.76$  Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 43.33 (s,  $\text{CH}_2\text{Cl}$ ), 127.75 (pent.,  $J_{\text{C-F}} = 0.8$  Hz,  $\text{ClCH}_2\text{CH}=\text{CH}$ ), 134.8 (pent.,  $J_{\text{C-F}} = 7.4$  Hz,  $\text{SF}_5\text{CH}=\text{CH}$ ), 137.38 (pent.,  $J_{\text{C-F}} = 1.1$  Hz,  $\text{SF}_5\text{CH}=\text{CH}-\text{CH}$ ), 142.4 (d.pent.,  $J_{\text{C-F}} = 20.7$  Hz,  $J_{\text{C-F}} = 1.6$  Hz,  $=\text{CHSF}_5$ ).

### Synthesis of 1-(pentafluoro- $\lambda^6$ -sulfanyl)hex-1,5-diene (34).

A mixture of potassium carbonate (4 g), 5-chloro-6-(pentafluoro- $\lambda^6$ -sulfanyl)hex-1-en (4.9 g, 0.02 mol) and 15 ml tetramethylene sulfone (sulfolane) was stirred at 65-70 $^{\circ}$ C for 4.5 h. After cooling to room temperature and filtration the crude product was removed from reaction mixture into a trap (cooling at -70 $^{\circ}$ C) at 30-40 $^{\circ}$ C/1-2 mm Hg. Redistillation gives 3.3g (80%) of 1-(pentafluoro- $\lambda^6$ -sulfanyl)hex-1,5-diene (34), b.p. 71-72  $^{\circ}$ C at 30 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.2 (m, 4H, 2CH $_2$ ), 5.18 (m, 2H, =CH $_2$ ), 5.73 (m, 1H, -CH=CH $_2$ ), 6.47 (m, 1H, CH=CHSF $_5$ );  $^{19}\text{F}$  NMR (188 MHz, CF $_3$ COOH,  $\text{CDCl}_3$ ):  $\delta$  = 161.8 (pent., 1F,  $J_{\text{F-F}}$  = 153.1 Hz). 140.7 (d, 4F,  $J_{\text{F-F}}$  = 153.1 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 29.71 (s, CH $_2$ ), 31.77 (pent.  $J_{\text{C-F}}$  = 0.9 Hz, CH $_2$ ), 116.12 (s, =CH $_2$ ), 136.16 (s, CH=), 138.24 (pent,  $J_{\text{C-F}}$  = 7.0 Hz, =C), 141.71 (d.pent,  $J_{\text{C-F}}$  = 19.6 Hz,  $J_{\text{C-F}}$  = 1.5 Hz, =CHSF $_5$ ).

### Synthesis of 1,5-di(pentafluoro- $\lambda^6$ -sulfanyl)hex-1,5-diene (35).

A mixture of potassium carbonate (5 g), 2,5-dichloro-1,6-di(pentafluoro- $\lambda^6$ -sulfanyl)hexane (4.1 g, 0.01 mol) and 15 ml DMF was stirred at 65-70 $^{\circ}$ C for 4.5 h. After cooling to room temperature and filtration, the DMF was removed from reaction mixture into a trap (cooling at -70 $^{\circ}$ C) at 30-40 $^{\circ}$ C/1-2 mm Hg. The crude product was distillation at 68-78 $^{\circ}$ C at 2 mm Hg. Redistillation gives 2.8g (85%) of 1,6-di(pentafluoro- $\lambda^6$ -sulfanyl)hexa-1,5-diene (35), b.p. 71-72  $^{\circ}$ C at 2 mm Hg.  $^1\text{H}$  NMR (200 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  = 2.33 (m, 4H, 2CH $_2$ ), 6.48 (m, 4H, , CH=CHSF $_5$ );  $^{19}\text{F}$  NMR (188 MHz, CF $_3$ COOH,  $\text{CDCl}_3$ ):  $\delta$  = 160.9 (pent., 1F,  $J_{\text{F-F}}$  = 153.6 Hz). 140.6 (d, 4F,  $J_{\text{F-F}}$  = 153.6 Hz);  $^{13}\text{C}$  NMR (50.3 MHz, TMC,  $\text{CDCl}_3$ ): 28.67 (s, CH $_2$ ), 136.37 (pent,  $J_{\text{C-F}}$  = 7.0 Hz, =C), 141.71 (d.pent,  $J_{\text{C-F}}$  = 19.9 Hz,  $J_{\text{C-F}}$  = 1.6 Hz, =CHSF $_5$ ).

#### 4. CONCLUSION.

An experimental facility for measuring the burning velocities and concentration flammability limits for gaseous fuel/air mixtures was designed and constructed.

Velocities of burning are determined for stoichiometric dimethyl ester of vethylphosphonic acid/air and triethylphosphate/air mixtures are 0.24 m/s and 0.31 m/s, respectively.

Influence of the fluorocontaining additives ( $\text{NF}_3$ ,  $\text{N}_2\text{F}_4$ ,  $\text{SF}_6$ ,  $\text{F}_5\text{S-R}$ ) on the speed and concentration limits of burning of phosphorus organic ester / air mixes is established. The addition of  $\text{NF}_3$  and  $\text{N}_2\text{F}_4$  increases the OPE burning velocities and expands the flammability ranges for phosphorus organic ester. The addition of  $\text{F}_5\text{S-R}$  reduces the OPE burning velocities and expands the flammability ranges for phosphorus organic ester. The addition of  $\text{SF}_6$  reduces the OPE burning velocities and flammability ranges for phosphorus organic ester.

We have shown that the reaction between the sulfur chloride pentafluoride ( $\text{F}_5\text{SCl}$ ) and unsaturated alcohols under irradiation of ultra-violet light leads to adducts of addition of  $\text{F}_5\text{SCl}$  to the double bounds in good yields. These adducts are useful precursors in the preparation of novel compounds containing pentafluorothio groups.

For the first time shown, that realization of reaction addition of sulfur chloride pentafluoride in the condition of photochemical or thermal reaction of addition, leads to formation of high strained cyclic compounds with sulfur pentafluoride groups in good yield.

We have found a high yield rout to mono- and di- adducts of  $\text{SF}_5\text{Cl}$  and 1,4-, and 1,5-alkadienes. These adducts are useful precursors in the preparation of earlier not known 1,3-,1,4- and 1,5-alkadienes with sulfur pentafluoride groups.

## 5. LITERATURE.

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